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Field and Laboratory Studies for the Development of Effluent Standards for the Steam Electric Power Industry

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16. ABSTRACT The report gives results of an evaluation of carbon absorption, chemical precipitation, reverse osmosis, and vapor compression distillation (VCD) as removal technologies for priority pollutants from wastewater streams of utility power plants. All but VCD were bench-scale tested for the removal of low concentration (1-50 ppb) pollutants from cooling tower blowdown and ash pond effluents at three coal-fired plants. The removal of organic pollutants (by activated carbon and reverse osmosis) and inorganic pollutants (by chemical precipitation and reverse osmosis) were evaluated at these plants. An operational VCD unit handling a combined waste stream was tested for the removal of both organic and inorganic pollutants at a fourth coal-fired plant. Samples of plant make-up water, cooling tower blowdown, ash pond effluent, and effluent waters from the treatment technologies were analyzed for priority organic and inorganic pollutants. Only eight pollutants were measured in concentrations greater than 10 ppb; none of these were common to all the plants studied. Carbon absorption and reverse osmosis removed priority pollutants, but low concentrations prevented definitive conclusions on their removal effectiveness. Chemical precipitation, reverse osmosis, and VCD effectively reduced low concentration inorganic compounds, including arsenic, copper, and lead, all of which were present in significant concentrations in at least one wastewater stream.

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ABSTRACT

Carbon absorption, chemical precipitation, reverse osmosis and vapor compression distillation (VCD) were evaluated as removal technologies for priority pollutants from wastewater streams of utility power plants. These technologies, except VCD, were tested in bench-scale systems for the removal of priority pollutants from cooling tower blowdown and ash pond effluent at three coal-fired plants. The removal of organic pollutants by activated carbon and reverse osmosis and inorganic pollutants by chemical precipitation and reverse osmosis was evaluated at these plants. An operational VCD unit handling a combined waste stream was tested for the removal of both organic and inorganic pollutants at a fourth coal-fired plant. Samples of plant make-up water, cooling tower blowdown and ash pond effluent plus effluent waters from the treatment technologies were analyzed for priority organic and inorganic pollutants.

Only eleven priority pollutants, of which eight were inorganic pollutants, were measured in concentrations greater than 10 ppb, and none of these were common to all the plants studied. Carbon absorption and reverse osmosis demonstrated some removal of priority organic pollutants, but the low concentrations observed prevented definitive conclusions on their removal effectiveness. Chemical precipitation, reverse osmosis, and vapor compression distillation effectively decreased the inorganic compounds including arsenic, copper and lead, all of which were present in significant concentration levels in at least one wastewater stream.

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SECTION 1

INTRODUCTION

The development and refinement of effluent limitations for the utility industry under the 1977 Clean Water Act Amendments places significant emphasis on the "priority" pollutants, some 129 compounds or species requiring removal from water effluents. The data concerning the presence and levels of these species in utility effluents are limited. However, based on preliminary data, several technologies have been identified which would potentially remove the priority pollutants at very low levels (Reference 1). Field data concerning the application of treatment technology to utility wastes were needed to establish whether treatment of dilute wastes is technologically feasible.

This report describes the results of bench-scale field tests conducted to evaluate the technical feasibility of reducing priority pollutants in utility wastewater streams. The following four processes were selected as having the highest potential for pollutant control based on a previous EPA study (Reference 1):

- Carbon adsorption
- Chemical precipitation
- Reverse osmosis
- Vapor compression distillation

Selection of these processes was based on several factors. Carbon adsorption is known to be effective for removal of organic materials at higher concentration levels than those generally observed in utility effluents. Similarly, chemical precipitation, i.e., lime or slufide, is practiced for the removal of high levels of trace elements. Reverse osmosis (RO) shows promise as a pretreatment step which produces a waste stream with concentrations in the range handled by conventional technology (i.e., reverse osmosis in conjunction with other treatments may effectively handle utility wastes). Vapor compression distillation (VCD) was selected because, although the technology is practiced effectively, no substantive information is available concerning the secondary pollution of VCD sludge or air emissions.

Bench-scale tests of carbon adsorption, chemical precipitation, and reverse osmosis were conducted at three coal-fired power stations to evaluate their performance in treating cooling tower blowdown and ash pond effluent. An operational vapor compression distillation unit processing plant wastewaters at a fourth coal-fired power station was sampled for secondary emissions. The results of the field tests and the procedures used in the evaluation are presented in the following sections of this report.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions resulted from the field evaluation of the performance of carbon adsorption, chemical precipitation, reverse osmosis and vapor compression distillation for the removal of priority pollutants from the wastewater streams of utility power plants.

- The wastewater streams at the power plants studied contained very low concentrations of priority pollutants. Only three organic and eight inorganic priority pollutants were measured in concentrations greater than 10 ppb. None of these compounds were consistently observed at concentrations greater than 10 ppb at all of the plants sampled.

- Within analytical ability to detect the low concentration levels, carbon adsorption and reverse osmosis significantly reduced the organic compound levels.

- Reverse osmosis and vapor compression distillation were effective in concentrating the priority pollutants in a wastewater stream and produced a clean water stream suitable for recycle.

- Chemical precipitation, reverse osmosis and vapor compression distillation were effective for the removal of inorganic compounds at the concentration levels encountered at the utility power plants. For arsenic, copper, and lead, lime precipitation and reverse osmosis demonstrated removal efficiencies greater than 50% when inlet concentrations are above 20 ppb. For the removal of selenium, reverse osmosis demonstrated a greater effectiveness than lime precipitation, 85 percent removal as compared to 24 percent. Vapor compression distillation effectively removed all priority inorganics with the exception of vanadium.

Little information concerning the presence, levels and frequency of occurrence of a number of priority pollutants in coal-fired power plants is available. Additional sampling by EPA under the Effluent Guidelines Division screening and verification analysis efforts should provide an adequate data base to supply this information.

Subsequent sampling and analysis efforts may identify priority pollutants occurring in concentrations requiring treatment. If this occurs, then further testing is warranted. The technologies examined in this study show sound potential which should be demonstrated on a pilot scale. At this stage, sufficient data would be developed to closely define treatment efficiency, practical operating parameters, and economics of installation for new plant and retrofit applications.

SECTION 3

RESULTS

The basic procedure followed to perform this study is presented in the first part of this section. A more detailed explanation of the test plan and analytical procedures is presented in the Appendix. A summary of results is presented at the end of the section.

3.1 PROCEDURE

The procedures for conducting the study can be divided into seven steps. These steps are listed below and an explanation of the objectives and procedures associated with each one follows.

1. Selection of technologies for evaluation

2. Selection of coal-fired power plants for sampling purposes

3. Development of test plans and field sampling procedures

4. Development of analytical procedures for laboratory analyses

5. Actual field testing of treatment technologies

6. Analyses of water samples

7. Interpretation of results

The first four steps involve the selection and conceptual development work associated with the project. The first step, selection of technologies, was provided by an earlier study, "Assessment of Technology for Control of Toxic Effluents from the Electric Utility Industry"(EPA Contract No. 68-02-2608, Work Assignment 9). Control technologies that showed the greatest promise for removing trace quantities of organic and inorganic priority pollutants from utility wastewaters were selected.

The second step involved selection of power plants as locations for conducting the field testing. The primary objective was to select plants known to, or likely to, contain at least some of the priority pollutants. With the assistance of the Utility Water Act Group (UWAG), Edison Electric Institute and other industry personnel, four plants were selected for testing based on plant operations and effluent compositions.

Concurrent with the efforts of selecting appropriate plant sites for testing, development of test plans for both laboratory and field testing was accomplished. The primary objective was to devise field evaluation plans for bench-scale systems that would answer the basic questions of the suitability of the chosen technology for removing the priority pollutants. No previous studies covering the types of compounds at the concentration levels expected were available to aid in the development of the evaluation plans. An essential element of the evaluation plans was that the field tests for each technology be simple and direct.

The problems of preserving sample integrity were evaluated to ensure that the analyses conducted at the laboratory accurately reflected the composition of the sample as it was collected in the field. To accomplish this, measures had to be taken to prevent sample contamination, chemical reaction and losses due to compound volatility. Several steps were taken to provide this assurance, such as prevention of any contamination from the materials used for sample collection, purging and collection of volatile organics in the field, and stabilization of samples by refrigeration and sample preparation. Once a complete set of procedures for each type of chemical analysis was developed, it was possible to begin the field evaluation.

For each sample taken, both organic and inorganic analysis was performed. Organic analysis was accomplished by use of both gas chromatography and gas chromatography-mass spectrometry. The plant inlet, cooling tower blowdown (CTB) and ash pond effluent (APE) samples were analyzed by gas chromatography-mass spectrometry to positively identify the presence of a compound. The faster and more economical gas chromatography was used to analyze the treated and untreated streams to evaluate the effectiveness of technologies for reducing pollutants. Evaluation of the success of treatment was based only on those compounds positively identified as present in the inlet streams. Most of the inorganic compounds were analyzed by atomic absorption. Selenium was analyzed by fluorometry and cyanide by a colorimetric procedure.

The field testing involved on-site sampling and demonstration of the treatment technologies. The equipment was loaded into a 40-foot trailer containing all the support equipment and laboratory space needed to perform the necessary field tasks. The chemical precipitation tests and activated carbon tests were performed in the trailer. The inlet wastewater samples from the cooling tower and ash pond were collected in large glass bottles that had been properly prepared to prevent contamination. The wastewater samples to be used as feed to the treatment technologies were analyzed for the complete list of priority pollutants. These analyses were used to determine the quality of the wastewater prior to treatment.

The reverse osmosis unit was operated at the sampling point and run for at least one hour prior to sampling of its outlet streams. During this time pH and conductivity measurements were taken for the inlet, the product and the reject stream. When these parameters reached steady-state, the sampling was performed.

The samples of the treated and untreated wastewater were collected, stored and shipped to the home laboratories. In the case of the purgeable organics, the samples were purged in the field to collect the organics prior to shipment.

The final step in the procedure was the analysis of the results. The development of detection limits and error limits was an important factor in analyzing the results and is explained in detail in the Appendix.

NUS Corporation, on behalf of UWAG, collected duplicate samples during the project testing and sampling. It is expected that those results will be available in the future for comparison.

3.2 SUMMARY OF DATA

A brief summary of the results of the study is presented in this section. The detailed results are presented in Section 6. A list of compounds observed in the plant inlet, the cooling tower blowdown and the ash pond effluent at the plants tested is presented. The results of testing the treatment technologies for removing the observed compounds in the two wastewater streams are presented. The results of the evaluation of the vapor compression distillation unit are presented last.

3.2.1 Water Samples for Plant Intake and Wastewater Streams

The compounds and concentrations observed at the three plants testing carbon adsorption, reverse osmosis, and chemical precipitation are presented in Table 3-1. The summary of organic compounds includes only those observed by gas chromatography and confirmed by gas chromatography-mass spectrometry. The concentration levels are those produced by gas chromatography analysis. A concentration preceded by "<" designates the detection limit for a compound which was identified but was present at a concentration too small to be quantified. A blank in the table signifies the compound was not identified as being present.

For comparison purposes, the EPA drinking water standards are presented in the table. Of the 29 concentrations of organic compounds presented in Table 3-1 (the phthalates are not included due to sample contamination), only those for dibromochloromethane, bromoform and toluene are greater than 10 ppb. For Plant 5409, more compounds were detected in the plant intake than were detected in the cooling tower blowdown and ash pond effluent.

TABLE 3-1. PRIORITY POLLUTANTS IDENTIFIED IN PLANT WATER STREAMS (ppb)

Organics[a]	Plant intake			Cooling tower blowdown			Ash pond effluent			EPA drinking water standards[b]	Irrigation standards[c]	Utility industry BATEA[d]
	Plant 5604	Plant 1226	Plant 5409	Plant 5604	Plant 1226	Plant 5409	Plant 5406	Plant 1226	Plant 5409			
Bromodichloromethane					8.2	2.6				100[e]		
Dibromochloromethane					58.5	<1.0		<1.0		100[e]		
Chloroform			1.4		<1.0	2.4	<1.0			0.5[f]		
Bromoform					134			<1.0		0.5[f]		
Carbon tetrachloride			<1.0							0.5[f]		
Trichloroethylene			<4.0			<4.0				0.5[f]		
Benzene	1.2		2.4			1.5	2.0		1.0			
Toluene	9.1		2.0	23.5			3.5		<1.0			
1,3/1,4-Dichlorobenzene			2.4/3.5							0.5		
1,2-Dichlorobenzene			5.3							0.5		
Bis(2-ethyl-hexyl) phthalate[g] or Benz(α)anthracene or Chrysene		*	*		*	*						
Diethyl phthalate	*											
Butyl benzyl phthalate												
Di-n-butyl phthalate	*	*	*	*	*	*						
Phenol			6.6						4.1			

TABLE 3-1. (Continued)

Inorganics[a]	Plant intake			Cooling tower blowdown			Ash pond effluent			EPA drinking water standards[b]	Irrigation standards[c]	Utility industry BATEA[d]
	Plant 5604	Plant 1226	Plant 5409	Plant 5604	Plant 1226	Plant 5409	Plant 5406	Plant 1226	Plant 5409			
Antimony	4	7	3	5	7	<1	6	7	5			
Arsenic	<1	3	<1	7	4	35(<1)	<1	9	74	50	1000	
Beryllium	<0.5	<0.5	<0.5	<0.5	<0.5	3.4	2.5	<0.5	<0.5		100	
Cadmium	<0.5	2.1	1.4	<0.5	1.8	0.8	1.0	2.0	<0.5	10	10	
Chromium	<2	7	<2	<2	5	37	4	6	<2	50	100	200
Copper	700	12	27	180	47	3800(620)	80	14	26	1000	200	1000
Lead	6	10	8	<3	3	130(70)	<3	4	<3	50	5000	
Mercury	<0.2	0.4	<0.2	<0.2	0.2	0.5	<0.2	<0.2	<0.2	2		
Nickel	< .5	1.5	1.7	6.0	6.0	4.0	9.5	5.5	2.5		200	
Selenium	<2	<2	<2	<2	<2	<2	3	8	42	10	20	
Silver	3	1.3	1.6	3	0.7	14	5.5	0.5	1.0	50	-	
Thallium	<1	<1	<1	<1	<1	8	1	1	9			
Vanadium	11	40	13	24	27	11	27	78	31			
Zinc	53	9	15	780	26	290(61)	300	7	11	5000	2000	1000

[a] Organic analysis by gas chromatography and confirmed presence by GC-MS.

[b] Federal Register, 24 December 1975 and 31 March 1977.

[c] Reference 2.

[d] Reference 3.

[e] Total Trihalomethanes.

[f] After treatment by granular activated carbon.

[g] Phthalates cannot be quantified due to sample contamination. * indicates compound identified.

[h] ( ) Parentheses indicate concentration of dissolved fraction.

[i] < - Designates concentration below detection limit.

The inorganics identified at the three plants are presented at the bottom of the table. As was done for the organic compounds, any concentration preceded by "<" designates a compound or element present below its detection limit. For comparison purposes, the EPA drinking water standards, as well as irrigation standards and current best available technology economically achievable (BATEA) regulations for the industry, are presented. Only arsenic, copper, lead, and selenium exceed any of the standards. These standards are presented only for comparison purposes; they do not represent proposed standards for priority pollutants at utility power plants.

3.2.2 Results of Treatment by Activated Carbon

The results of the chemical analysis for the inlet and outlet streams of the activated carbon column are summarized in Table 3-2. In 8 cases out of 20, a compound was identified in the inlet at a concentration greater than the detection limit. In only two cases, both for toluene, did the effluent contain a compound at a concentration greater than the detection limit. For the most part, observed removal efficiencies were greater than 50%. However, it should be noted that at such very low inlet concentrations, the lack of detection in the outlet and the correspondingly high removal efficiencies are not unusual.

3.2.3 Results of Treatment by Chemical Precipitation

The results of the chemical analyses for selected inorganics in the influent and effluent samples for lime precipitation are presented in Table 3-3. The table also contains the results of treating cooling tower blowdown and ash pond effluent with lime and with lime plus ferrous sulfate. The results for

TABLE 3-2. SUMMARY OF ACTIVATED CARBON PERFORMANCE FOR ORGANIC COMPOUNDS[a]

Compound	Inlet concentration (ppb)	Outlet concentration (ppb)	Observed removal efficiency (%)
Benzene			
Plant 5604 (CTB)[c]	<1[b]	<1	—
Plant 5604 (APE)[d]	2.0	<1	>50
Plant 5409 (CTB)	1.5	<1	>33
Plant 5409 (APE)	<1	<1	—
Toluene			
Plant 5604 (CTB)	23.5	3.0	87
Plant 5604 (APE)	3.5	7.0	—
Plant 5409 (APE)	<1		—
Ethylbenzene			
Plant 5604 (APE)	<1	<1	—
Chloroform			
Plant 5604 (APE)	<1		—
Plant 1226 (CTB)	<1		—
Plant 5409 (CTB)	2.4		>58
Plant 5409 (APE)	<1	<1	—
Bromodichloromethane			
Plant 1226 (CTB)	8.2		>88
Plant 5409 (CTB)	2.6		>62
Dibromochloromethane			
Plant 1226 (CTB)	58.5		>98
Plant 1226 (APE)	<1		—
Plant 5409 (CTB)	<1		—
Bromoform			
Plant 1226 (CTB)	154		>99
Plant 1226 (APE)	<1		—
Trichloroethylene			
Plant 5409 (CTB)	<4		—

[a] A blank in the column signifies the compound was not identified as being present.
[b] < - Designates concentration below detection limit
[c] CTB - Cooling tower blowdown
[d] APE - Ash pond effluent

TABLE 3-3. SUMMARY OF CHEMICAL PRECIPITATION PERFORMANCE FOR INORGANIC COMPOUNDS (Lime/lime plus ferrous sulfate)[a]

Compound	Inlet concentration (ppb)	Outlet concentration (ppb)	Observed removal efficiency (%)
Arsenic			
Plant 5604 (CTB)[c]	7	<1/<1[b]	>86/>86
Plant 5604 (APE)[d]	<1	<1/<1	--/--
Plant 1226 (CTB)	4	3/3	25/25
Plant 1226 (APE)	9	<1/3	>89/67
Plant 5409 (CTB)	<1	2.5/<1	--/--
Plant 5409 (APE)	75	<1/<1	>99/>99
Copper			
Plant 5604 (CTB)	180	48/26	73/86
Plant 5604 (APE)	80	23/23	71/71
Plant 1226 (CTB)	47	18/<4	62/>91
Plant 1226 (APE)	14	10/7	29/50
Plant 5409 (CTB)	620	70/48	89/92
Plant 5409 (APE)	26	12/18	54/31
Lead			
Plant 5604 (CTB)	<3	<3/<3	--/--
Plant 5604 (APE)	<3	<3/<3	--/--
Plant 1226 (CTB)	<3	5/<3	--/--
Plant 1226 (APE)	4	<3/<3	>25/>25
Plant 5409 (CTB)	70	<3/<3	>96/>96
Plant 5409 (APE)	<3	<3/<3	--/--
Selenium			
Plant 5604 (CTB)	<2	<2/<2	--/--
Plant 5604 (APE)	3	3/3	0/0
Plant 1226 (CTB)	<2	<2/<2	--/--
Plant 1226 (APE)	8	8/7	0/13
Plant 5409 (CTB)	<2	2.3/<2	--/--
Plant 5409 (APE)	42	52/32	--/24

[a] Separates values for lime and lime plus ferrous sulfate respectively
[b] < - Designates concentration is below detection limit
[c] CTB - Cooling tower blowdown
[d] APE - Ash pond effluent

arsenic, copper, lead, and selenium are presented because of their relatively high concentration in at least one wastewater stream.

In general, chemical precipitation using lime was very effective for reducing these compounds. The notable exception was selenium. Ferrous sulfate was added with lime to evaluate coprecipitation as a mechanism for reducing inorganics. For the cases studied, lime plus ferrous sulfate exhibited the same or only slightly higher removal than lime alone.

In other tests, lime plus ferric sulfate was evaluated for possible enhanced removal of arsenic and chromium. Lime plus sodium sulfide was also analyzed for enhanced cadmium and mercury removal. In only one case, for chromium at Plant 1226, was an increased reduction in concentration achieved over lime precipitation alone. The inlet concentrations at this plant were very low, however, 4 ppb and 6 ppb in the cooling tower blowdown and ash pond effluent, respectively. These results are presented in more detail in Section 6.

3.2.4 Results of Treatment by Reverse Osmosis

The results of the chemical analyses for removal of organic compounds by reverse osmosis are presented in Table 3-4. The data in the table demonstrate the effectiveness of reverse osmosis in removing most of the eight compounds presented. Removal of toluene was the only exception. In general, the inlet concentrations were too low to produce definitive results.

The results of the analysis for removal of inorganics by reverse osmosis are summarized in Table 3-5. Concentrations of most of the compounds were significantly reduced by this

TABLE 3-4. SUMMARY OF REVERSE OSMOSIS PERFORMANCE FOR ORGANIC COMPOUNDS[a]

Compound	Inlet concentration (ppb)	Outlet concentration (ppb)	Observed removal efficiency (%)
Benzene			
Plant 5604 (CTB)[c]	<1[b]		--
Plant 5604 (APE)[d]	2.0	1.4	30
Plant 5409 (CTB)	1.5	<1	33
Plant 5409 (APE)	<1	<1	—
Toluene			
Plant 5604 (CTB)	23.5	20.5	13
Plant 5604 (APE)	3.5	2.8	20
Plant 5409 (APE)	<1	3.3	—
Ethylbenzene			
Plant 5604	<1	2.1	—
Chloroform			
Plant 5604 (APE)	<1	<1	—
Plant 1226 (CTB)	<1	<1	—
Plant 5409 (CTB)	2.4	<1	>58
Plant 5409 (APE)	<1	<1	—
Bromodichloromethane			
Plant 1226 (CTB)	8.2		>88
Plant 5409 (CTB)	2.6		>62
Dibromochloromethane			
Plant 1226 (CTB)	58.5	<1	>98
Plant 1226 (APE)	<1	<1	—
Plant 5409 (CTB)	<1		—
Bromoform			
Plant 1226 (CTB)	154	<1	>99
Plant 1226 (APE)	<1	<1	—
Trichloroethylene			
Plant 5409 (CTB)	<4	<4	—

[a] A blank in the column signifies the compound was not identified as being present.

[b] < - Designates concentration below detection limit

[c] CTB - Cooling tower blowdown

[d] APE - Ash pond effluent

TABLE 3-5. SUMMARY OF REVERSE OSMOSIS PERFORMANCE FOR INORGANIC COMPOUNDS

Compound	Inlet concentration (ppb)	Outlet concentration (ppb)	Observed removal efficiency (%)
Arsenic			
Plant 5604 (CTB)[a]	7	49	—
Plant 5604 (APE)[b]	<1[c]	<1	—
Plant 1226 (CTB)	4	<1	>75
Plant 1226 (APE)	9	<1	>89
Plant 5409 (CTB)	<1	<1	—
Plant 5409 (APE)	75	<1	>99
Copper			
Plant 5604 (CTB)	180	32	82
Plant 5604 (APE)	80	9	89
Plant 1226 (CTB)	47	10	79
Plant 1226 (APE)	14	10	29
Plant 5409 (CTB)	620	51	92
Plant 5409 (APE)	26	9	65
Lead			
Plant 5604 (CTB)	<3	20	—
Plant 5604 (APE)	<3	<3	—
Plant 1226 (CTB)	<3	<3	—
Plant 1226 (APE)	4	<3	>25
Plant 5409 (CTB)	70	<3	>96
Plant 5409 (APE)	<3	6.5	—
Selenium			
Plant 5604 (CTB)	<2	<2	—
Plant 5604 (APE)	3	<2	>33
Plant 1226 (CTB)	<2	<2	—
Plant 1226 (APE)	8	<2	>75
Plant 5409 (CTB)	<2	<2	—
Plant 5409 (APE)	42	6.1	85

[a] CTB - Cooling tower blowdown

[b] APE - Ash pond effluent

[c] < - Designates concentration below detection limit

technology. A comparison of this table with Table 3-3 indicates that reverse osmosis was more effective than chemical precipitation for the removal of selenium. It was also as effective for removing the other compounds.

3.2.5 Results of Vapor Compression Distillation Performance

The vapor compression distillation (VCD) unit sampled at Plant 3009 was analyzed for the removal of both organic and inorganic compounds. The concentrations of the few organic compounds observed were very low and no definitive results were obtained. The analysis of inorganics was definitive. High concentrations of copper (2,700 ppb), vanadium (1,000 ppb) and zinc (910 ppb) were observed in the inlet to the unit. Most were removed from the wastewater and concentrated in the brine reject stream. The only significant concentration of a compound in the product stream was vanadium (590 ppb).

SECTION 4

PLANT CHARACTERIZATION AND SAMPLING LOCATIONS

Background information characterizing the plants studied is presented in this chapter. The characterization includes the size of the plant, the type of coal burned, flue gas clean-up methods, and detailed descriptions of the water supply and wastewater streams which were sampled. The sampling points used in each plant are also identified.

The coal-fired power plants studied were all baseload facilities. All employed cooling towers for heat rejection and ash ponds for disposal of fly ash. A summary of the data pertinent to the study for each plant is presented in Table 4-1.

4.1 PLANT WATER/WASTEWATER CHARACTERIZATIONS AND LOCATION OF SAMPLE POINTS

The water and wastewater streams studied are described in this section. Particular emphasis was placed on identifying all wastewater streams entering the ash pond systems. For Plants 5604, 1226, and 5409, the cooling water systems and ash ponding systems are described. For Plant 3009 the sampling concerned only the VCD units and the wastewater stream going into the unit.

4.1.1 Plant 5604

Water/Wastewater Characterization--

The plant water/wastewater system can be divided into three major parts:

TABLE 4-1. SUMMARY OF PLANT CHARACTERISTICS

Plant	Total generating capacity	Fuel	Flue gas cleanup	
5604	4 units, 750 MW	Sub-bituminous coal	Electrostatic precipitators,	Mechanical draft cooling tower for unit 4
		Ash, 12%	Wet venturi unit 4	Once-through mechanical draft cooling - winter months, units 1, 2 & 3
		Sulfur, 0.5%		Mechanical draft cooling tower for summer months
1226	7 units, 1229 MW	Natural gas units 1, 2 & 3	Electrostatic precipitators	Mechanical draft cooling tower for unit 6
		Fuel oil: units 4 & 5		Mechanical draft cooling tower for unit 6
		Ash content of fuel oil, 0.06%		
		Coal: units 6 & 7		
		Illinois bituminous coal		
		Ash, 11%		
5409	3 units, 2900 MW	Coal (numerous suppliers)	Electrostatic precipitators	Natural draft cooling towers - one for each unit
		Ash, 15% Sulfur, 1.0%		
3009	2 units, 716 MW	Sub-bituminous coal	Combined scrubbers (fly ash and SO_2 removal)	Mechanical draft cooling
		Ash, 6.1-12.6% Sulfur, 0.4-1.0%		

1. A once-through cooling water system which provides the cooling for three of the plant's four generating units. A cooling tower is used during the summer months.

2. A recirculating cooling water system which uses a cooling tower to provide the cooling duty.

3. Four ash ponds make up the ash ponding system. The system is composed of two separate systems. Two of the ash ponds serve Units 1, 2, and 3, and two ash ponds plus a clear pond serve Unit 4.

Makeup water for both cooling systems comes from the nearby river. The water is chlorinated prior to in-plant use. The cooling towers are usually operated between 3 and 4 cycles of concentration. Water from the clear pond is used to sluice bottom ash from the four boilers. The ash sluice water is returned to the ash ponds. Makeup water to the venturi scrubbers is also taken from the clear pond and the blowdown from the scrubber water system is sent to the ash ponds.

Boiler blowdown, roof and yard drainage, coal pile runoff, and demineralizer regeneration wastes are all disposed in the ash ponds for Units 1, 2, and 3. Metal cleaning wastes are either hauled off-site or disposed in the ash disposal area. Figure 4-1 is a general flow diagram of the plant water/wastewater systems for Units 1, 2, and 3. Figure 4-2 covers all water systems for Unit 4.

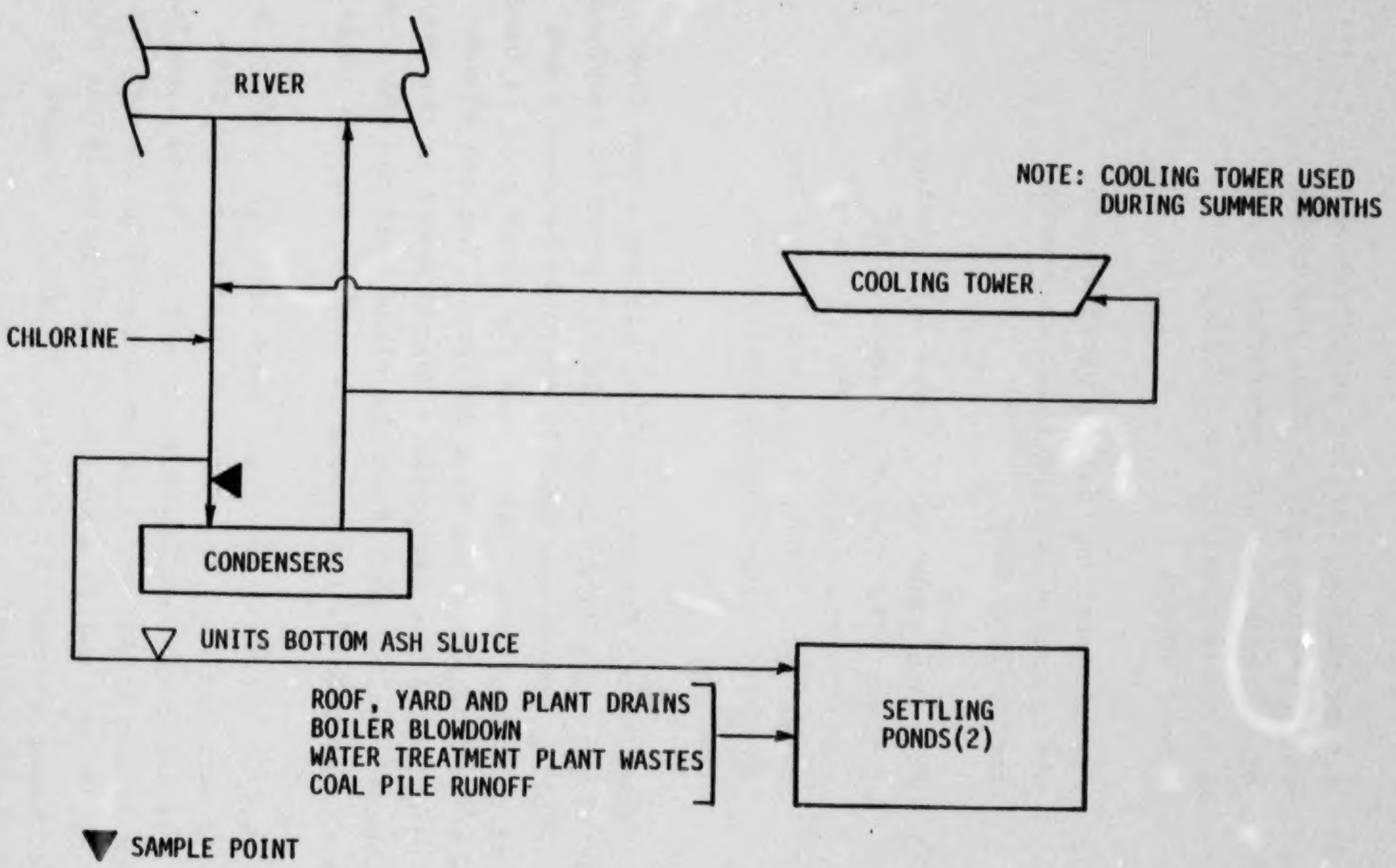

Figure 4-1. General water flow diagram of water/wastewater system for Units 1, 2, and 3 of Plant 5604.

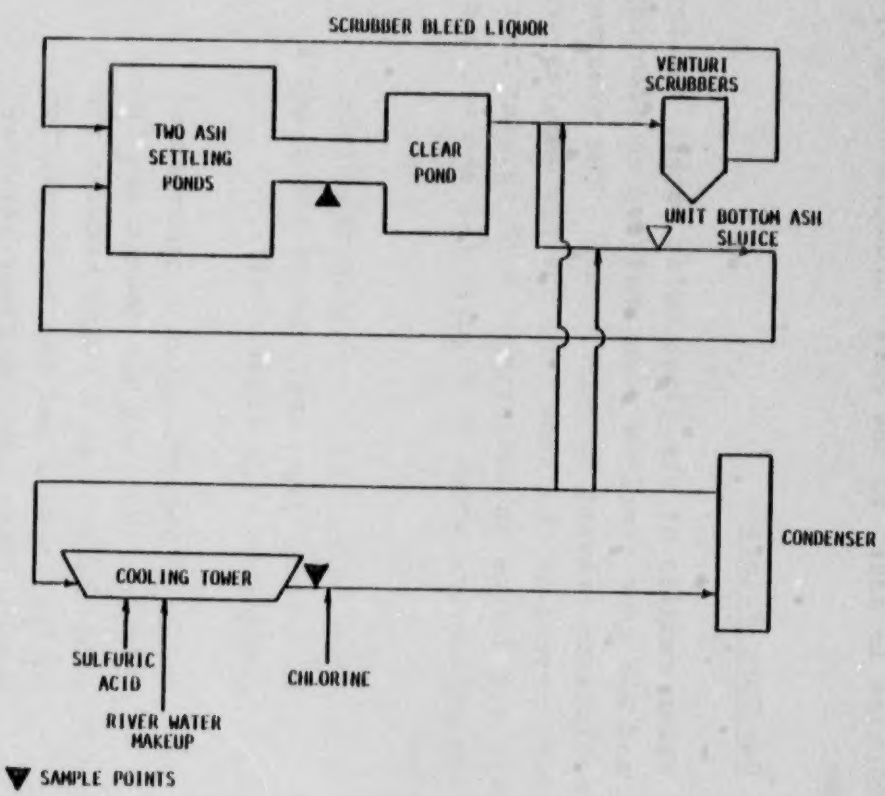

Figure 4-2. General water flow diagram of water/wastewater system for Unit 4 of Plant 5604.

Various chemicals are added to the plant water/wastewater system. Chlorine is added to the plant intake water. Chemicals added to the boiler water include sodium hydroxide, hydrazine, and phosphate. Chlorine, sulfuric acid, a commercial biocide, and lime are added to the recirculating cooling system water. Chlorine is added to the once-through cooling system when in use.

Sampling Points--

Water samples of the plant inlet water, cooling tower blowdown, and ash pond overflow were analyzed to identify the priority pollutants present in each stream. The treatment technologies were tested at the same time the raw samples were taken to eliminate variations in composition with respect to time. The sampling points are shown in Figures 4-1 and 4-2 and are listed below:

- Plant Inlet Water - inside the plant at a point just upstream of the plant's condensers (see Figure 4-1).

- Cooling Tower Blowdown - upstream of chlorine addition but downstream from acid addition at a point between the cooling towers and the recirculation pumps. This cooling tower services Unit 4 only.

- Ash Pond Effluent - at dewatering pumps from ash pond just before clear pond.

4.1.2 Plant 1226

Plant Water/Wastewater Characterization--

The plant water/wastewater system is made up of three major components:

1. A once-through cooling water system with a cooling tower downstream for temperature control before discharge. This system provides the cooling for Units 1 through 5.
2. A recirculating cooling water system with cooling towers providing the cooling for Units 6 and 7.
3. An ash sluicing system which includes one ash pond for allowing ash and other settleable matter to be removed from the ash sluice water from Units 4, 5, 6, and 7 as well as from other plant effluent streams.

Makeup water for both cooling systems comes from a local river. Ash sluice water is taken from the recirculating cooling water system and piped to the ash pond for disposal. A blowdown stream from the recirculating cooling system is piped directly to the ash pond.

Those waste streams sent to the ash pond include demineralizer regeneration wastes, floor drains, coal pile runoff, and laboratory drains. Metal cleaning wastes containing copper are discharged to a lined pond where they are aerated and neutralized with lime. A polymer is added to enhance settling of the precipitated copper. Figure 4-3 is a general flow diagram of the plant water/wastewater system.

Daily additions of chlorine are made to the plant recirculating cooling water system for the control of biological growth within the system. The chlorine is added during two 30-minute periods, one in the morning and one in the afternoon. The quantity of chlorine added during each period is 156 pounds.

Sampling Points--

Water samples of the plant inlet water, cooling tower blowdown, and ash pond overflow were analyzed to identify the priority pollutants present in each stream. The treatment technologies were tested at the same time as the raw samples were taken, eliminating time variable problems. These sampling points are shown in Figure 4-3 and are listed below:

- Plant Inlet Water - at the inlet pipe discharge into the cooling tower basin.
- Cooling Tower Blowdown - upstream of the cooling water recirculating pumps and immediately before the chlorine and sulfuric acid addition points.
- Ash Pond Overflow - at the pond outfall.

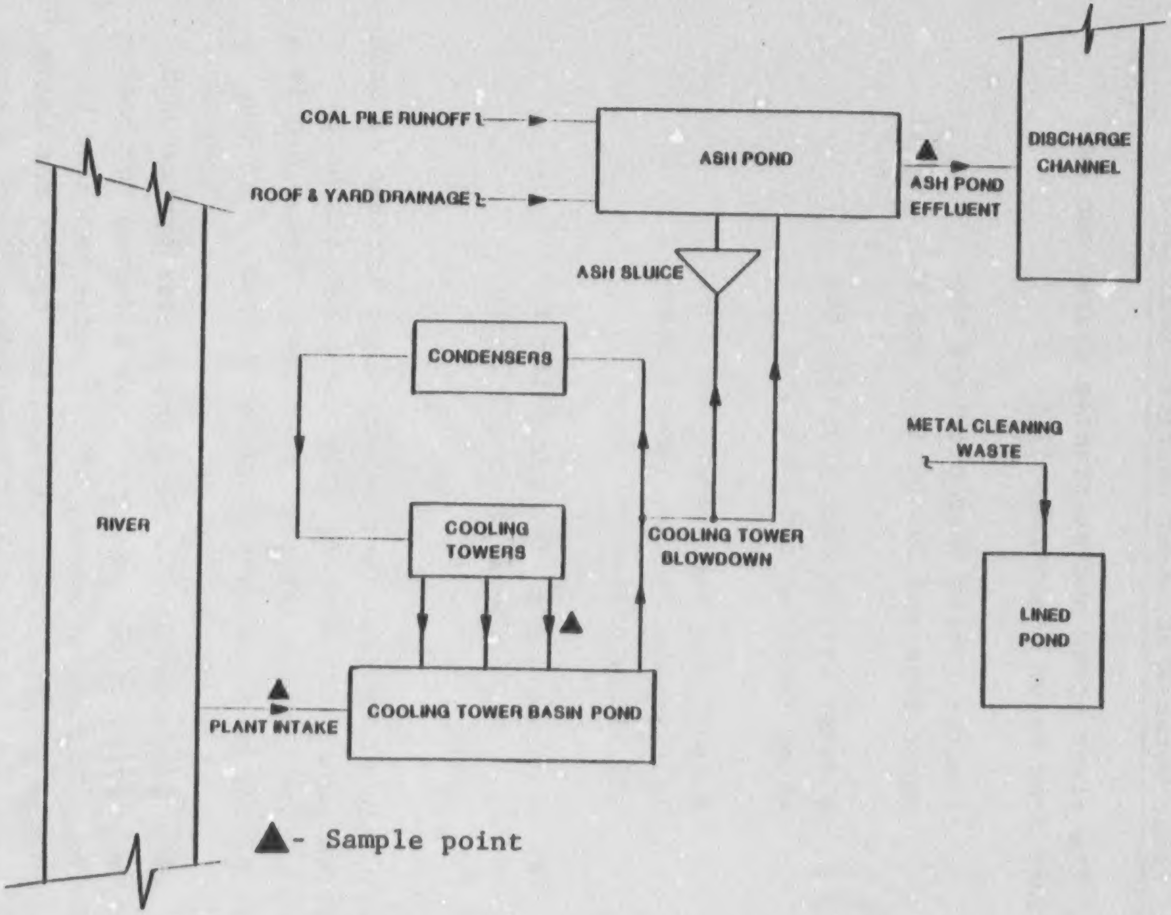

Figure 4-3. General flow diagram of plant water/wastewater system for Plant 1226.

4.1.3 Plant 5409

Plant Water/Wastewater Characterization--

The plant water and wastewater system can be divided into four major components:

1. A water system that provides the water required for Units 1 and 2.

2. A water system that provides the water required for Unit 3.

3. A dual pond arrangement for receiving the primary wastes from all three units.

4. A fly ash pond for receiving fly ash sluice water from all three units.

At present, the plant has river makeup water intakes at each of the three cooling towers and only one plant discharge which comes from the fly ash pond overflow. Figure 4-4 is a schematic of the plant water/wastewater system.

The subsystem for Units 1 and 2 uses pyrite wash water and a portion of the cooling tower blowdown for bottom ash sluicing. On rare occasions, river water may also be used for bottom ash sluicing. The cooling towers for Units 1 and 2 are hyperbolic natural draft structures having a combination asbestos/cement fill. Average circulation, blowdown, and makeup rates are given in Table 4-2. All primary wastewater

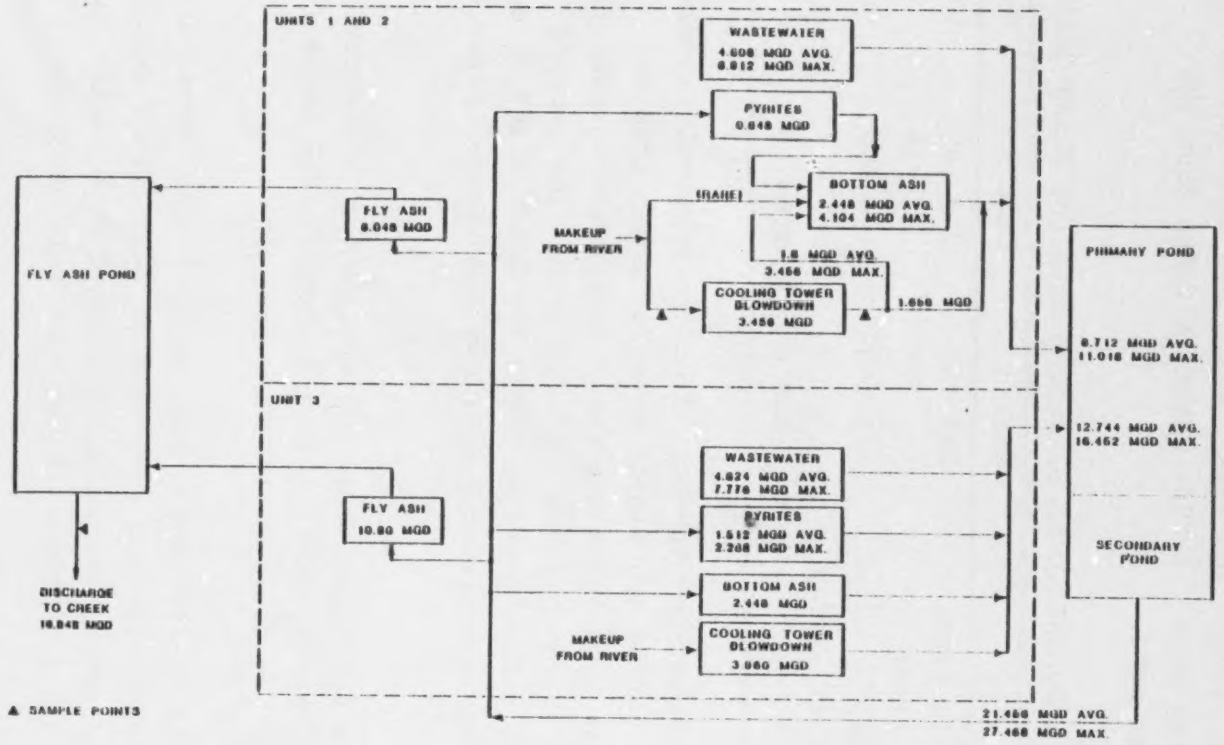

Figure 4-4. Plant 5409 water/wastewater system.

streams, such as bottom ash sluice, pyrite water, cooling tower blowdown, sumps, and area runoff, are sent to the primary settling pond. Pyrite water is taken from the secondary clear pond.

TABLE 4-2. COOLING TOWER OPERATING DATA FOR PLANT 5409

	Unit 1	Unit 2	Unit 3
Circulation rate (gpm)	248,000	248,000	600,000
Blowdown rate (gpm)	770	770	1,300
Makeup rate (gpm)	4,600	4,600	8,000
Average number of cycles	7	7	7
pH	7.4-7.6	7.4-7.6	7.4-7.6

The subsystem for Unit 3 has no internal recycle streams. All bottom ash sluice water is taken from the secondary clear pond and all primary wastewater streams are sent directly to the primary settling pond. The cooling tower for Unit 3 is similar to those for Units 1 and 2, but larger. Average circulation, blowdown, and makeup rates are given in Table 4-2.

Flue gas cleaning is accomplished with electrostatic precipitators (ESP). Fly ash from the ESP units is sluiced to the fly ash pond.

Other wastestreams, such as coal pile runoff and metal cleaning wastes, are also sent to the primary settling pond. Metal cleaning wastes are generated from boiler tube cleanings, which are scheduled for each unit about every two years.

Water from the secondary clear pond is used for sluicing fly ash from the electrostatic precipitators to a large fly ash holding pond. The overflow from the fly ash pond is discharged to a nearby creek. At present, this outlet is the only discharge from the entire plant water and wastewater system.

The only chemical additions to the plant water system are chlorine and sulfuric acid. Both chemicals are added to the cooling water system at the inlet to the recirculating pumps which are located between the cooling tower basin and the condensers. Chlorination for algae control is done once a day, Monday through Saturday, for a one-hour period. The injection rates for chlorine are usually 250 lb/hr for Units 1 and 2 and 333 lb/hr for Unit 3. Sulfuric acid (93%) is continuously added to control the pH of the cooling water. The pH is maintained between 7.4 and 7.6.

The boilers at Plant 5409 are designed to operate at supercritical temperatures with ultra-pure feedwater. No blowdown of boiler water is required. The ultra-pure feedwater is obtained from a seven-step water treatment process utilizing demineralizers. The only waste stream from the demineralizers comes from regeneration of the cation and anion resins which is an intermittent process.

Sampling Points--

Sampling was done at three separate points within Plant 5409. These points are shown on Figure 4-4 and described below:

- Plant Makeup - taken at the pump which supplies river water to the Unit 2 cooling tower.

- Cooling Tower Effluent - taken at the Unit 2 cooling tower basin immediately upstream of the recirculating pumps.

- Ash Pond Effluent - taken at the pond outlet to the creek.

4.1.4 Plant 3009

Plant Water/Wastewater Characterization--

The plant water system is designed for zero aqueous discharge. Water losses occur through cooling tower evaporation and drift, scrubber evaporation, pond evaporation, solids occlusion, and boiler losses. Plant makeup water is taken from a nearby river. Figure 4-5 is a schematic of the plant water system. All continuous wastewater streams from the plant are piped to the vapor compression distillation (VCD) units where the product water is returned to the plant for reuse and the reject stream is ponded.

Vapor Compression Distillation--

Two vapor compression distillation units at Plant 3009, designed by the Research Conservation Corporation, came onstream in late spring and summer of 1976. A diagram of the VCD unit is provided in Figure 4-6. The sample points are indicated on this diagram.

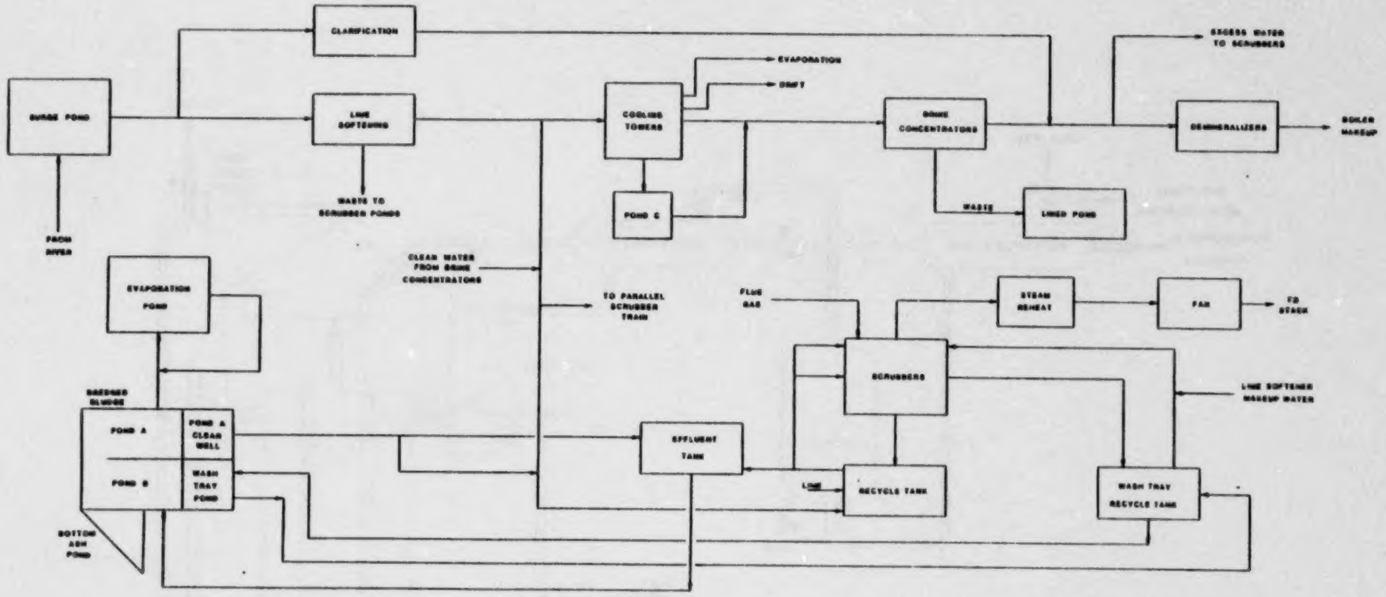

Figure 4-5. Plant 3009 water flow scheme.

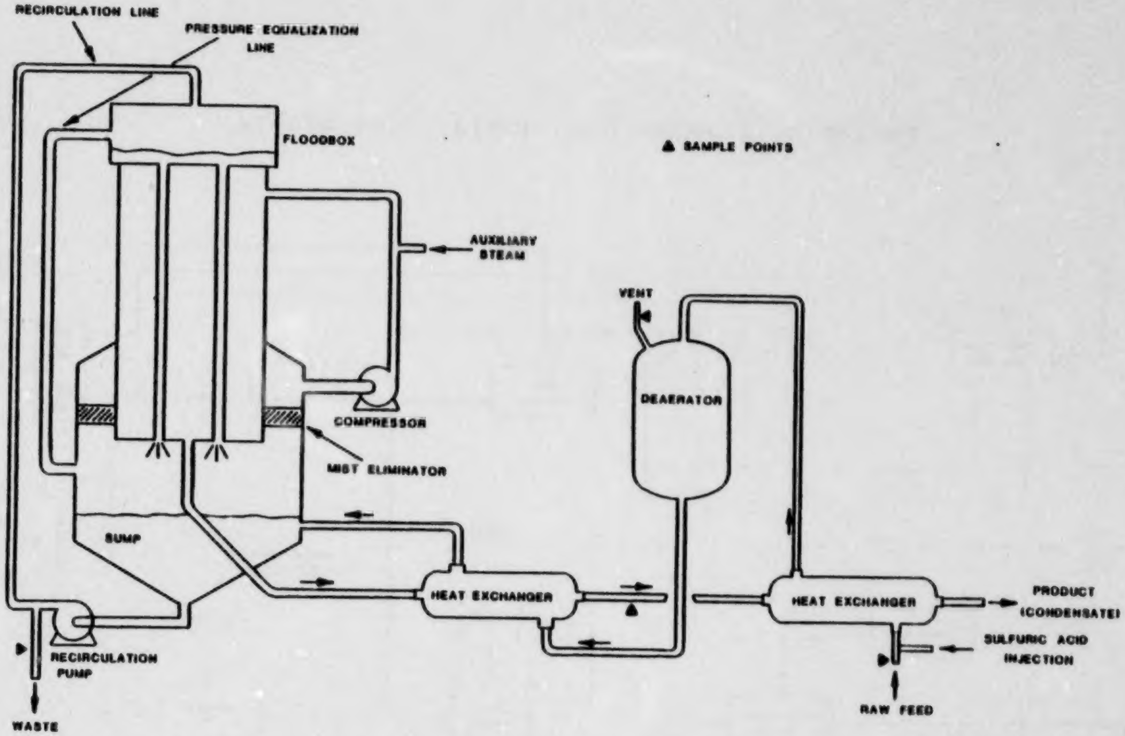

Figure 4-6. Vapor compression distillation unit.

Each unit is designed for a raw feed of 175 gpm and a 98.8% product recovery rate. This design produces a brine waste stream of approximately 2.1 gpm. At the time of the sampling, the waste stream flow was slightly higher than normal, averaging 2.5 to 3.0 gpm. Plant personnel attributed the higher waste rate to a higher solids content in the raw feed.

Feed to the VCD unit is supplied by cooling tower blowdown (CTB) and/or a CTB surge pond (Pond C) as shown on Figure 4-5. Inlet temperatures vary with the feed source. The feed is treated with sulfuric acid for pH adjustment and heated in a product heat exchanger prior to deaeration. No data were available on the amount of steam loss from the deaerator vent, but estimated overall steam consumption for each VCD unit is 400 lb/hr of medium pressure steam.

From the deaerator, the feed undergoes heat exchange with the product stream before entering the sump of the VCD unit. The sump temperature is about 209°F. Vapors rising from the sump pass through a mist eliminator to remove any entrained brine or other liquid contaminants. The water vapor is then compressed and fed into the condenser.

Brine is pumped from the sump into the floodbox and descends through the condenser tubes by gravity flow. Water vapor, condensing on the outside of the tubes, heats the brine, which partially evaporates before returning to the sump. The condensed water is drawn off through a product line and run through two exchangers in series for feed reheat. Temperature of the product stream averages 109-194°F. The product water is either sent to demineralizers for boiler makeup, SO_2 scrubbers, or the recycle tank. A constant brine level is maintained in the sump by pumping a small amount of brine from the VCD recycle line to one of two lined two-acre ponds.

Sampling Points--

Samples were taken at four separate points on VCD Unit A. These points, shown on Figure 4-6, were:

- Raw feed inlet prior to sulfuric acid injection.
- Product condensate after the primary heat exchanger.
- Brine waste directly below the sump.
- Vent gas from the deaerator.

During the sampling period, all raw feed was supplied from Pond C and contained no blowdown directly from the cooling towers.

SECTION 5

CHEMICAL ANALYSIS OF UNTREATED WATER SAMPLES

The results of the laboratory analyses of the untreated water streams are presented in this section. The results are organized to emphasize both the types of compounds and the concentrations encountered at the different plants. For each of three plants, 5604, 1226, and 5409, the data characterize the inlet water to the plant, the cooling tower blowdown and the ash pond effluent. The inlet streams to the plants were analyzed to provide a comparison of the pollutant concentrations entering the plants with those in the plant wastewaters. For Plant 3009, the inlet stream to the vapor compression distillation unit was characterized for inorganic compounds. As GC-MS confirmations were not run for the VCD inlet stream, the organic analyses for the VCD unit are not positive identifications.

5.1 ORGANIC COMPOUNDS

The inlet and wastewater streams were characterized for priority organic compounds by gas chromatography (GC) analysis and gas chromatography-mass spectrometry (GC-MS) analysis. The GC-MS was used to positively identify compounds that were tentatively identified by the GC analysis. The limitations of the two methods of analysis and the significance of the concentrations determined by each are discussed in detail in the Appendix. For the purposes of data presentation, the results of the GC analyses are presented in this section. However, as GC analysis does not positively identify the presence of a compound, it was concluded that the compound was not present unless confirmed by the GC-MS analysis.

Both the GC and GC-MS results for the analysis of organic compounds are presented in Tables 5-1 through 5-6 for plants 5604, 1226, and 5409. The concentrations observed by the two instruments were usually different, as can be seen in the tables. The sensitivity to concentrations of a given compound is different for GC and GC-MS; therefore, variations exist in concentrations presented in the two tables for a given compound. The difficulty of resolving the sensitivity of the instruments at the very low concentrations observed contributed to the differences in concentration. In many instances a concentration was measured but was below the defined detection limit. This meant that the compound was present but at such a low concentration that it could not be quantified. A concentration preceded by "<" designates the detection limit for a compound which was identified but was present at a concentration too low to be quantified. A blank in the tables signifies that a compound was not identified as being present. The results of the GC analysis of the inlet stream to the VCD unit at Plant 3009 are not included as no GC-MS confirmation was performed on this sample. The sampling at this plant was done only as a means of evaluating VCD performance.

The results of the analysis for organic priority pollutants at Plant 5604, presented in Table 5-1, indicate that the intake stream to the plant was relatively clean. The only notable concentration was for toluene, which was just below 10 ppb. A comparison of the compounds present in the plant inlet with those in the cooling tower blowdown stream and the ash pond effluent indicates that most of the compounds found in the wastewater streams were present in the inlet. The differences

TABLE 5-1. PLANT 5604: ORGANIC ANALYSES OF RAW WATER SAMPLES BY GAS CHROMATOGRAPHY (Concentrations in ppb)[a]

Compound	Sample stream Plant make-up	 Cooling tower blowdown	 Ash pond effluent
Chloroform			<1[b]
Benzene	1.2	<1	2.0
Toluene	9.1	23.5	3.5
Ethylbenzene			<1
Phenol	No sample	2.4[c]	No sample
Dimethyl Phthalate[d]	*	*	No sample
Diethyl Phthalate	*	*	No sample
Fluoranthene		2.0	No sample
3,4 Benzofluoranthene or 11,12 Benzofluoranthene		4.0	No sample
Di-n-butyl Phthalate	*	*	No sample

[a] A blank in the table signifies that a compound was not identified as being present.

[b] < - Designates concentration below detection limit.

[c] Evaporated - redissolved residue.

[d] Phthalates cannot be quantified due to sample contamination.

TABLE 5-2. PLANT 5604: ORGANIC ANALYSIS OF RAW WATER SAMPLES BY GAS CHROMATOGRAPHY - MASS SPECTROMETRY (Concentrations in ppb)[a]

Compound	Sample stream		
	Plant make-up	Cooling tower blowdown	Ash pond effluent
Chloroform	0.3		0.2
Bromoform	0.1		
Trichloroethylene	16	8.3	19
Tetrachloroethylene		0.5	0.6
Benzene	0.9		0.8
Toluene	0.5	0.7	0.7
Ethylbenzene	0.5		
Di-n-butyl Phthalate	1.0	7.7	1.6
Bis(2-ethylhexyl) Phthalate			1.0
Butyl Benzyl Phthalate	1.4	50	
Diethyl Phthalate	1.0		4.9

[a] A blank in the table signifies that a compound was not identified as being present.

TABLE 5-3. PLANT 1226: ORGANIC ANALYSES OF RAW WATER SAMPLES BY GAS CHROMATOGRAPHY (Concentrations in ppb)[a]

Compound	Sample stream		
	Plant make-up	Cooling tower blowdown	Ash pond effluent
Chloroform	<1[b]	<1	
Bromodichloromethane		8.2	
Dibromochloromethane		58.5	<1
Bromoform		154	<1
Tetrachloroethylene		<2	<2
Benzene		3.8	
Toluene			<1
Phenol	4.1	1.7	2.0
Dimethyl Phthalate[c]	*	*	
Diethyl Phthalate	*		
Butyl Benzyl Phthalate	*		
Bis(2-ethylhexyl) phthalate or 1,2 Benzanthracene or Chrysene	*	*	
Di-n-butyl Phthalate	*	*	*
Hexachlorocyclopentadiene	<1		<1
γ BHC or δ BHC (Benzenehexachloride)		<1	

[a] A blank in the table signifies that a compound was not identified as being present.

[b] < - Designates concentration below detection limit.

[c] Phthalates cannot be quantified due to sample contamination.

TABLE 5-4. PLANT 1226: ORGANIC ANALYSIS OF RAW WATER SAMPLES BY GAS CHROMATOGRAPHY - MASS SPECTROMETRY (Concentrations in ppb)[a]

Compound	Sample stream		
	Plant make-up	Cooling tower blowdown	Ash pond effluent
Bromodichloromethane		13	
Bromoform		54	2.2
Chloroform		3.3	
Dibromochloromethane		53	0.7
1,1,1-Trichloroethane	0.8		0.8
Bis(2-ethylhexyl) phthalate	5.2	1.2	1.3
Di-n-butyl Phthalate	15	4.8	9.4

[a] A blank in the table signifies that a compound was not identified as being present.

TABLE 5-5. PLANT 5409: ORGANIC ANALYSES OF RAW WATER SAMPLES BY GAS CHROMATOGRAPHY (Concentrations in ppb)[a]

Compound	Sample stream		
	Plant make-up	Cooling tower blowdown	Ash pond effluent
1,1 Dichloroethane	$<1^{b}$		
Chloroform	1.4	2.4	<1
1,2 Dichloroethane	<1		
Carbon Tetrachloride	<1		
Bromodichloromethane		2.6	
1,2 Dichloropropane	<1		
Trichloroethylene	<4	<4	
Dibromochloromethane		<1	
Benzene	2.4	1.5	1.0
Toluene	2.0		<1
Phenol	6.6	4.1	4.1
Dimethyl Phthalate[c]		*	*
Diethyl Phthalate		*	
Fluoranthene	<1	1.0	
Butyl Benzyl Phthalate		*	
Bis(2-ethylhexyl) Phthalate or 1,2 Benzanthracene or Chrysene	*	*	
Acenaphthylene[d]	5		
Acenaphthene[d]			
Di-n-butyl Phthalate	*	*	*
1,3 Dichlorobenzene	2.4	1.0	
1,4 Dichlorobenzene	3.5		
Hexachloroethane or 1,2 Dichlorobenzene	5.3		
Bis(2-Chloro-Isopropyl) Ether or Bis(2-Chloro-Ethyl) Ether	<1		1.2

TABLE 5-5
(Cont.)

Compound	Sample stream Plant make-up	 Cooling tower blowdown	 Ash pond effluent
Hexachlorocyclopentadiene		<1	
4 Bromophenyl Ether or α BHC		<1	
γ BHC or δ BHC (Benzenehexachloride)			<1
Aldrin			<1
Heptachlor Epoxide		<1	
α Endosulfan		<1	
Dieldrin or DDE		<1	
Endrin			<1
DDT			<1

[a] A blank in the table signifies that a compound was not identified as being present.

[b] < - Designates concentration below detection limit.

[c] Phthalates cannot be quantified due to sample contamination.

[d] Merged peaks.

TABLE 5-6. PLANT 5409: ORGANIC ANALYSIS OF RAW WATER SAMPLES BY GAS CHROMATOGRAPHY - MASS SPECTROMETRY (Concentrations in ppb)[a]

Compound	Sample stream		
	Plant make-up	Cooling tower blowdown	Ash pond effluent
Bromodichloromethane		3.1	
Carbon Tetrachloride	1.1		
Chloroform	1.5	11	
Dibromochloromethane		0.3	
1,1,2,2-Tetrachloroethane	0.5	0.5	0.3
Trichloroethylene	0.6	0.6	
Benzene	2.3	0.6	0.6
Ethylbenzene		0.6	
Toluene	1.6	0.9	0.8
Phenol	0.5		0.4
1,3 and 1,4-Dichlorobenzene	0,9		
1,2-Dichlorobenzene	8.5		
Hexachlorobenzene	0.6		
Bis(2-ethylyhexyl) Phthalate	14	5.7	7.1
Di-n-butyl Phthalate	2.2	3.3	6.1

[a] A blank in the table signifies that a compound was not identified as being present.

in observed concentration levels can generally be attributed to the cycles of concentration which were 4 for the cooling tower and 2.6 for the ash pond.

Several phthalates were observed; however, these are believed to be the result of sample contamination occurring in a filtering step during sample preparation. No significance is attached to the indicated presence of these compounds due to the contamination.

The GC-MS analysis detected several compounds that were not observed by the GC analysis. These included chloroform, carbon tetrachloride, bromochloromethane and bromoform in the plant inlet stream. The GC-MS measured concentration levels were low, less than 3 ppb in all cases. Significant concentrations of trichloroethylene were observed in both the cooling tower blowdown and the ash pond effluent by the GC-MS. It is not known why these compounds were not observed by the GC.

The results of the analysis for organics at Plant 1226 are presented in Tables 5-3 and 5-4. Several volatile organics were observed in the cooling tower blowdown at this plant. The river intake was clean, however. It should be noted that the water intake to this plant is in a tidal estuary and the quality of the intake water varies both diurnally and seasonally. As a result, the quality of the water in the plant at any given time may be appreciably different from the water coming into the plant. The concentration levels observed for dibromochloromethane and bromoform were high, 59 ppb and 154 ppb, respectively. Trace quantities of these were also observed in the ash pond water. Phthalates were also measured; however, these were probably filter contaminants as discussed earlier.

The results of the analyses for organics at Plant 5409 are presented in Tables 5-5 and 5-6. There were 15 compounds observed in the river intake to this plant. Only eight were confirmed by GC-MS analysis. Of these only benzene, phenol, 1,3 dichlorobenzene, 1,4 dichlorobenzene and 1,2 dichlorobenzene were observed at concentrations greater than 2 ppb. Most of the compounds observed in the cooling water and ash pond water were measured at or near the same concentration levels as in the plant inlet water. Several compounds were seen in the cooling water and ash pond water that were not seen in the plant intake.

5.2 INORGANIC COMPOUNDS

Each sample of water was analyzed for 15 inorganic priority pollutants. In addition to these compounds, chlorides, pH, suspended solids and total organic carbon were identified for each sample. Chlorides were included as a means of estimating the concentration factor. This was done by comparing the chlorides in the ash pond or cooling basin to the level in the intake water. Total suspended solids, pH, and total organic carbon were included as standard parameters for characterizing water and wastewater streams.

The untreated water streams for plant 5604, 1226, and 5409 are presented in Tables 5-7 through 5-9. The inorganic analysis of the feed stream to the VCD unit at Plant 3009 is presented in Table 5-10.

The results of the analysis for inorganic compounds at Plant 5604, Table 5-7, indicate that the most significant concentrations encountered were for copper and zinc. In general, the inlet concentrations for the species presented in the table

TABLE 5-7. PLANT 5604: INORGANIC ANALYSIS OF RAW WATER SAMPLES (Concentrations in ppb unless otherwise noted)

	Plant intake water	Cooling tower blowdown	Ash pond effluent
Antimony	4	5	6
Arsenic	<1.0 [a]	7	<1.0
Beryllium	<0.5	<0.5	2.5
Cadmium	<0.5	<0.5	1.0
Chromium	<2.0	<2.0	4
Copper	700	180	80
Lead	6	<3.0	<3.0
Mercury	<0.2	<0.2	<0.2
Nickel	<0.5	6.0	9.5
Selenium	<2.0	<2.0	3
Silver	3	3	5.5
Thallium	<1.0	<1.0	<1.0
Vanadium	11	24	27
Zinc	53	780	300
Cl^-	14 ppm	57 ppm	37 ppm
CN^-	4	3	22
pH		6.9	5.6
Total Suspended Solids		42 ppm	15 ppm
Total Organic Carbon	5.5 ppm	14 ppm	7.6 ppm

[a] < - Designates concentration is below detection limit.

TABLE 5-8. PLANT 1226: INORGANIC ANALYSIS OF RAW WATER SAMPLES (Concentrations in ppb unless otherwise noted)

	Plant intake water	Cooling tower blowdown	Ash pond effluent
Antimony	7	7	7
Arsenic	3	4	9
Beryllium	<0.5[a]	<0.5	<0.5
Cadmium	2.1	1.8	2.0
Chromium	7	5	6
Copper	12	47	14
Lead	10	3	4
Mercury	0.4	0.2	<0.2
Nickel	1.5	6.0	5.5
Selenium	<2.0	<2.0	8
Silver	1.3	0.7	0.5
Thallium	<1.0	<1.0	<1.0
Vanadium	40	27	78
Zinc	9	26	7
Cl^-	360 ppm	490 ppm	790 ppm
CN^-	7	5	<1
pH		6.8	9.1
Total Suspended Solids		3 ppm	9 ppm
Total Organic Carbon	20 ppm	20 ppm	<20 ppm

[a] < - Designates concentration is below detection limit.

TABLE 5-9. PLANT 5409: INORGANIC ANALYSIS OF RAW WATER SAMPLES (Concentrations in ppb unless otherwise noted)

	Plant intake water	Cooling tower blowdown	Ash pond effluent
Arsenic	<1.0 [a]	35(<1.0)[b]	74
Antimony	3	<1.0	5
Beryllium	<0.5	3.4	<0.5
Cadmium	1.4	0.8	<0.5
Chromium	<2.0	37	<2.0
Copper	27	3800(620)	26
Lead	8	130(70)	<3.0
Mercury	<0.2	0.5	<0.2
Nickel	1.7	4.0	2.5
Selenium	<2.0	<2.0	42
Silver	1.6	14	1.0
Thallium	<1.0	8	9
Vanadium	13	11	31
Zinc	15	290(61)	11
Cl^-		110 ppm	28 ppm
CN^-	5 ppm	5	13
pH		6.8	6.7
Total Suspended Solids	5	460 ppm	14 ppm
Total Organic Carbon	20 ppm	21 ppm	<20 ppm

[a] < - Designates concentration is below detection limit.

[b] Parenthesis indicates concentration of dissolved fraction.

TABLE 5-10. RESULTS OF INORGANIC ANALYSIS FOR INLET WATER TO VAPOR COMPRESSION DISTILLATION UNIT, PLANT 3009 (Concentrations in ppb unless otherwise noted)

	Inlet to VCD
Antimony	7
Arsenic	50
Beryllium	<0.5 [a]
Cadmium	1
Chromium	5
Copper	2,675
Lead	7
Mercury	2
Nickel	3
Selenium	<2.0
Silver	15
Thallium	<1.0
Vanadium	1,000
Zinc	906
CN^-	24
TOC (ppm)	20

[a] < - Designates concentration is below detection limit.

are low (less than 10 ppb) with the exception of copper and zinc. The concentrations in the cooling tower blowdown show slight increases in arsenic and nickel. These increases are just slightly larger than would be expected from the cycles of concentration of the makeup water. The cycles of concentration for the cooling tower water were 4, while the ash pond showed 2.6 based on the chloride concentration. Vanadium increased slightly but was lower in the cooling tower water and ash pond water than would be expected from the concentration effect. The concentration of zinc showed a fifteen-fold increase over the inlet while copper decreased by a factor of about one-fourth. The concentrations of the species in the ash pond effluent were slightly higher than observed in the cooling tower blowdown. Beryllium, cadmium, chromium, nickel, selenium, silver, vanadium, and cyanide in the ash pond effluent increased just slightly as compared to cooling tower blowdown and plant inlet water. The copper concentration was considerably lower in the ash pond effluent than in both the inlet water and the cooling tower blowdown. The zinc concentration in the ash pond was lower than that observed in the cooling tower blowdown but higher than the inlet water.

The intake water to Plant 1226, shown in Table 5-8, was very clean with only copper and vanadium existing in concentrations greater than 10 ppb. Copper and zinc concentrations increased slightly in the cooling tower water as compared to that at the plant intake. The increases were higher than would be expected from the 1.4 cycles of concentration observed at the time of the sampling. The vanadium concentration in the cooling water decreased noticeably as compared to the plant intake water.

The copper concentration in the ash pond was approximately the same while the vanadium concentration in the ash pond was twice as high as the intake. The cycles of concentration for the ash pond as compared to the plant intake were 2.2.

The results of the analysis for inorganics at Plant 5409, presented in Table 5-9, are somewhat unusual. While the concentrations in the plant inlet were comparable to the other two plants, the cooling tower blowdown contained higher concentrations of arsenic, copper, lead and zinc. However, when a sample of this water was filtered through a 10-micron filter, well over 75 percent of the material was removed. This was interpreted to mean that the metals were present as suspended particulate matter. The removal efficiencies calculated in Section 6.0 were based on the dissolved fraction in the untreated cooling tower water. The concentration of 37 ppb of chromium in the cooling tower blowdown is higher than the other plants. At the time of the sampling, the concentration factor for the cooling water over the intake water was 7.3.

Arsenic, selenium and vanadium were present in significant concentrations in the ash pond effluent. The arsenic concentration of 74 ppb was present as dissolved matter and could have entered the system as a component of the fly ash. The selenium concentration of 42 ppb was also significant as its concentration in the plant inlet water and the cooling tower blowdown was below the detection limit of the analytical procedure. The concentration of vanadium in the ash pond, 31 ppb, was approximately as expected based on the inlet concentration of 13 ppb and 2 cycles of concentration.

The data presented in Table 5-10 characterize the feedwater stream to the vapor compression distillation unit at

Plant 3009. This stream contains wastewater from all sections of the plant. Of particular note are the observed concentrations of copper, vanadium, and zinc, which were the highest observed in the study (for an untreated wastewater stream). The arsenic concentration, 50 ppb, was also noteworthy. As this plant was included only for the purpose of evaluating VCD performance, no plant intake samples were analyzed for comparison purposes.

SECTION 6

CONTROL EVALUATION

This section presents the data resulting from the field evaluation of each of the four treatment technologies. These data are organized according to organic and inorganic analysis for the four field test sites. Each analysis itemizes the compounds identified as being present in the cooling tower blowdown or ash pond effluent before and after treatment by the respective control technologies. The types of analyses presented for each control technology are:

- Activated carbon - organics only
- Chemical precipitation - inorganics only
- Reverse osmosis - organics and inorganics
- Vapor compression distillation - organics and inorganics

In addition to quantifying organic and inorganic compounds, each control technology was evaluated for its efficiency in removing these compounds. The removal efficiencies were calculated using the following equation:

$$E = \frac{C_i - C_o}{C_i} \times 100$$

where E = observed removal efficiency (%)
C_i = inlet concentration
C_o = outlet concentration

At each plant, the inlet concentration of a particular wastewater stream was characterized for all control technologies by one grab sample. For example, one sample of untreated ash pond water was analyzed to determine the inlet conditions for the activated carbon columns, the reverse osmosis unit, and the chemical precipitation tests.

In many cases, circumstances did not allow the calculation of a removal efficiency. Such cases occurred when the inlet concentration was at or below the detection limit for the compound or when the observed outlet concentration was greater than the inlet concentration. In all cases, the results of the analyses for compounds in both the inlet and outlet are presented whether or not a removal efficiency is calculated and, in the case of organic analysis, whether or not the compound was confirmed by GC-MS.

A more detailed description of the sampling techniques, field testing procedures, and laboratory analysis procedures and accuracies is presented in the Appendix.

6.1 ACTIVATED CARBON

The field testing of activated carbon to evaluate removal of trace organics was accomplished using 0.5-inch ID glass columns packed with 60 inches of Calgon Filtrasorb 400 granular activated carbon. By using a constant displacement pump, a continuous feed of 10 ml/min was maintained during the performance testing and resulted in a liquid residence time of about 14 minutes. The activated carbon was washed with nitric acid prior to being packed in the columns. This procedure lessened the chance of sample contamination by ash material in the carbon.

Tables 6-1 through 6-3 present the results of the chemical analyses for organic compounds in the outflow from the carbon columns at each of the plants tested. Each table contains both the cooling tower blowdown and ash pond effluent results for the plants tested.

The results for Plant 5604 are presented in Table 6-1. Only one compound was observed in a concentration greater than 10 ppb. Toluene was observed at 23.5 ppb in the cooling tower blowdown. Activated carbon reduced the concentration to 3.9 ppb, a reduction of 83 percent. The toluene concentration measured in the exit from the column was higher than the inlet for the ash pond effluent sample. In general, the inlet concentrations of the few compounds present were so low that little or no removal was observed.

The results for Plant 1226 are summarized in Table 6-2. Several compounds were observed in the inlet sample for cooling tower blowdown but not observed as being present in the effluent. These were bromodichloromethane, dibromochloromethane, bromoform, and benzene. It is not known whether these compounds were effectively eliminated or whether the wastewater sample used for evaluation was of different composition than the sample representing inlet conditions. As shock chlorination was being performed at the time of sampling, it is possible that the sample analyzed to represent inlet conditions was of different quality than the inlet sample to the carbon column.

The results for Plant 5409 are presented in Table 6-3. Although 13 compounds were identified as being present in the cooling tower water, only six were measured above the detection limit. In addition, only five compounds were confirmed by GC-MS analysis. Of these five compounds, only one (benzene) was

TABLE 6-1. PLANT 5604: REMOVAL OF ORGANIC COMPOUNDS BY ACTIVATED CARBON (Concentrations in ppb)[a]

Compounds	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Chloroform				<1✓[b,c]		--
Benzene	<1✓	<1	--	2.0✓	<1	>50
Toluene	23.5✓	3.9	83	3.5✓	7.0	--
Ethylbenzene				<1✓		--
Phenol	2.4[d]	N/A[e]	--		N/A	--
Dimethyl phthalate[f]	*		--		*	--
Diethyl phthalate	*	*	--		*	--
Fluoranthene	2.0	1.1	45		*	--
Butyl benzyl phthalate		*	--		*	--
Bis (2 ethylhexyl) phthalate or 1,2 benzanthracene or chrysene		*	--		*	--
3,4 benzofluoranthene or 11,12 benzo-fluoranthene	4	3.6	10			
Di-n-butyl phthalate	*	*	--		*	--
Pyrene		1.5	--			
Benzo (α) pyrene		<1	--			

[a] A blank in the table signifies that a compound was not identified as being present.

[b] ✓ - Indicates that presence of this compound was confirmed by GC-MS.

[c] < - Designates concentration below detection limit.

[d] Evaporated - redissolved residue.

[e] N/A - Not analyzed.

[f] Phthalates cannot be quantified due to sample contamination.

TABLE 6-2. PLANT 1226: REMOVAL OF ORGANIC COMPOUNDS BY ACTIVATED CARBON (Concentrations in ppb)[a]

Compounds	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
1,2,4 Trichlorobenzene or hexachlorobutadiene				<1 [b]		--
γ BHC or δ BHC (Benzenehexachloride)	<1 [c]		--			
Chloroform	<1✓		--			
Bromodichloromethane	8.2✓		>88			
Dibromochloromethane	58.5✓		>98	<1✓		--
Bromoform	154✓		>99	<1✓		--
Tetrachloroethylene	<2		--	<2		--
Benzene	3.8		>74			
Toluene				<1		--
Ethylbenzene					2.3 [d]	--
Phenol	1.7	N/A [e]	--	2.0	N/A	--
Dimethyl phthalate [f]	*					
Fluoranthene		<1	--			
Bis (2 ethylhexyl) phthalate or 1,3 benzanthracene or chrysene	*	*	--		*	--
3,4 Benzofluoranthene or 11,12 benzofluoranthene		1.0	--			
Di-n-butyl phthalate	*	*	--	*	*	--

[a] A blank in the table signifies that a compound was not identified as being present.
[b] ✓ - Designates concentration below detection limit.
[c] < - Indicates that presence of this compound was confirmed by GC-MS analysis.
[d] Questionable identification and concentration.
[e] N/A - Not Analyzed.
[f] Phthalates cannot be quantified due to sample contamination.

TABLE 6-3. PLANT 5409 REMOVAL OF ORGANIC COMPOUNDS BY ACTIVATED CARBON (Concentrations in ppb)[a]

Compounds	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Dimethyl phthalate[b]	*		--	*		--
Diethyl phthalate	*	*	--			
Fluoranthene	1.0	<1[c]	--		2.3	
Butyl benzyl phthalate	*		--			
Bis (2 ethylhexyl) phthalate or 1,2 benzanthracene or chrysene	*	*	--		*	
Di-n-butyl phthalate	*	*	--	*	*	
Pyrene		<1	--		1.6	--
1,3 Dichlorobenzene	1.0	1.8	--			
Bis (2-chloro-isopropyl) ether or bis (2-chloroethyl) ether				1.2		>17
Hexachlorocyclopentadiene	<1		--			
4 Bromophenyl ether or α BHC	<1		--			
γ BHC or δ BHC (benzene-hexachloride)		<1	--	<1		--
Aldrin				<1		--
Heptachlor epoxide	<1		--			
α Endosulfan	<1		--			
Dieldrin or DDE	<1		--			
Endrin				<1		--

TABLE 6-3.
(Cont.)

Compounds	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
DDT				<1		--
1,1 Dichloroethane		<1	--		<1	--
Chloroform	2.4✓[d]		>58	<1	<1	--
1,2 Dichloroethane					<1	--
Bromodichloromethane	2.6✓		>62			
1,2 Dichloropropane						
Trichloroethylene	<4✓		--	--		
Dibromochloromethane	<1✓		--			
Benzene	1.5✓	<1	>33	1.0✓	<1	--
Toluene		<1	--	<1✓		--
Phenol	4.1	N/A[e]	--	4.1✓	N/A	--

[a] A blank in the table signifies that a compound was not identified as being present.
[b] Phthalates cannot be quantified due to sample contamination.
[c] < - Designates concentration below detection limit.
[d] ✓ - Indicates that presence of this compound was confirmed by GC-MS analysis.
[e] N/A - Not Analyzed.

identified in the carbon column effluent and it was reduced below the detection limit. In the ash pond effluent nine compounds were identified as being present, but only three were confirmed by GC-MS analysis. Again, these compounds were either reduced below the detection limit or completely eliminated by the activated carbon. In general, the very low inlet concentrations for most compounds in both wastewater streams make it difficult to evaluate the removal efficiencies of this technology.

6.2 CHEMICAL PRECIPITATION

Four chemicals were used in batch precipitation tests performed with sample water from both of the waste streams tested. Lime was used as the primary precipitating agent, with ferrous sulfate tested for possible enhanced removal from coprecipitation mechanisms. In addition, ferric sulfate and sodium sulfide were tested to examine their effect upon specific metals. Ferric sulfate was examined for arsenic and chromium removal. Sodium sulfide was examined for cadmium and mercury removal.

6.2.1 Lime Precipitation

Tables 6-4 through 6-6 present the results of the analyses for inorganic compounds for the treatment of cooling tower blowdown and ash pond effluent by lime precipitation. The tables also provide a percent removal for compounds where appropriate.

The results reported in Table 6-4 for Plant 5604 indicate chemical precipitation with lime was effective in decreasing the concentrations of arsenic, copper, and zinc. These metals were present in concentrations significantly higher than the detection limit. The results for nickel were inconclusive. The nickel concentration in the effluent of the cooling tower

TABLE 6-4. PLANT 5604: INORGANIC REMOVAL EFFICIENCIES FOR LIME PRECIPITATION (Lime, pH = 11.5) (Concentrations in ppb unless otherwise noted)

	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Arsenic	7	1	>86	<1[a]	<1	--
Antimony	5	3	40	6	5	17
Beryllium	<0.5	<0.5	--	2.5	<0.5	>80
Cadmium	<0.5	<0.5	--	1	<0.5	>50
Chromium	<2	<2	--	4	<2	>50
Copper	180	48	73	80	23	71
Lead	<3	<3	--	<3	<3	--
Mercury	<0.2	<0.2	--	<0.2	<0.2	--
Nickel	6	12	--	9.5	<0.5	>95
Selenium	<2	<2	--	3	3	0
Silver	3	4	--	5.5	5	9
Thallium	<1	<1	--	<1	<1	--
Vanadium	24	77	--	27	17	37
Zinc	780	140	82	300	31	90
Total Organic Carbon[b]	<20			<20		

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[a] < - Designates concentration below detection limit.

[b] Values are in ppm.

TABLE 6-5. PLANT 1226: INORGANIC REMOVAL EFFICIENCIES FOR LIME PRECIPITATION (Lime, pH = 11.5) (Concentrations in ppb unless otherwise noted)

	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Arsenic	4	3	25	9	<1 [a]	>89
Antimony	7	4	43	7	10	--
Beryllium	<0.5	0.9	--	<0.5	<0.5	--
Cadmium	1.8	3.0	--	2.0	2.1	--
Chromium	5	9	--	6	11	--
Copper	47	18	62	14	10	29
Lead	3	5	--	4	<3	>25
Mercury	0.2	0.7	--	<0.2	0.3	--
Nickel	6.0	2.9	52	5.5	6.0	--
Selenium	<2	<2	--	8	8	0
Silver	0.7	0.9	--	0.5	0.4	20
Thallium	<1	<1	--	<1	<1	--
Vanadium	27	6	78	78	78	0
Zinc	26	2	92	7	<2	>71
Total Organic Carbon [b]	<20	<20		<20	<20	

[a] < - Designates concentration below detection limit.

[b] Values are in ppm.

TABLE 6-6. PLANT 5409: INORGANIC REMOVAL EFFICIENCIES FOR LIME PRECIPITATION (Lime, pH = 11.5) (Concentrations in ppb unless otherwise noted)

	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Arsenic	<1	3	--	74	<1	>99
Antimony	<1	4	--	5	4	20
Beryllium	3.4	0.8	76	<0.5	<0.5	--
Cadmium	0.8	<0.5	>38	<0.5	<0.5	--
Chromium	37	9	76	<2	<2	--
Copper	620	70	89	26	12	54
Lead	70	<3	>96	<3	<3	--
Mercury	0.5	0.3	40	<0.2	<0.2	--
Nickel	4	2.3	43	2.5	2.2	12
Selenium	<2	2	--	42	52	--
Silver	14	7.8	44	1	1.1	--
Thallium	8	<1	>88	9	8	11
Vanadium	11	6	45	31	19	39
Zinc	61	3	95	11	<2	>82
Total Organic Carbon	21	<20	>5	<20	<20	

[a]< - Designates concentration below detection limit.

[b]Values are in ppm.

blowdown was greater than the inlet value. However, 95 percent of the nickel was removed from the ash pond. For vanadium the outlet concentration from the cooling tower blowdown sample was higher than the inlet value, while 37 percent removal was observed for the ash pond sample. Lime precipitation also demonstrated some removal of beryllium, cadmium and chromium in the ash pond sample. The other species were at or below the detection limits.

The results of the analyses of the water samples treated by lime only for Plant 1226 are presented in Table 6-5. In general, the inlet concentrations for both cooling tower blowdown and ash pond effluent are very low. However, the data show that lime precipitation was effective in reducing the concentrations of copper, nickel, vanadium, and zinc in the cooling tower blowdown. Interestingly, lime precipitation had no effect on the vanadium concentration in the ash pond effluent. The data indicate good arsenic removal from the ash pond effluent, but are too limited to judge the effectiveness of lime precipitation for removing the other metals.

Table 6-6 presents the results of the inorganic analyses for the treatment of cooling tower blowdown and ash pond effluent by lime precipitation for Plant 5409. In general, both inlet streams were fairly clean. Significant concentrations were observed for chromium, copper, lead and zinc in the cooling tower blowdown, while arsenic, selenium and vanadium were the more significant compounds in the ash pond effluent. The data indicate that lime precipitation was effective in removing arsenic, chromium, copper, lead and zinc. Some removal of beryllium and mercury was observed, but the inlet concentrations were too low to make any firm judgments. In some cases, the outlet concentration for a metal exceeded the inlet concentration.

This discrepancy occurred for selenium in the analysis for both the cooling tower blowdown and ash pond effluent. The concentration differences are relatively small and may be attributed to the measurement limitations of the detection equipment.

6.2.2 Lime Plus Ferrous Sulfate Precipitation

Tables 6-7 through 6-9 present the results of lime plus ferrous sulfate precipitation tests for the removal of inorganic compounds from the cooling tower blowdown and ash pond effluent of the three plants tested. Ferrous sulfate was added to evaluate the influence of coprecipitation mechanisms on the removal effectiveness.

A comparison of Tables 6-4 and 6-7 (Plant 5604) shows that, in most cases, the combination of lime and ferrous sulfate had equivalent or higher observed removal efficiencies than lime alone. For instance, the observed removal of copper and zinc from a sample of cooling tower blowdown was definitely increased from 73 percent to 86 percent for copper and from 82 percent to 95 percent for zinc. In general, the removal efficiencies were higher, but not dramatically so. One notable exception to this generality is antimony, for both cooling tower blowdown and ash pond effluent. The evidence for increased antimony removal through lime plus ferrous sulfate precipitation from evaluation of the data is not conclusive.

A comparison of Tables 6-5 and 6-8 (Plant 1226) shows that little or no improvement in removal efficiency (lime plus ferrous sulfate over lime alone) can be concluded from the data. The removal of copper did increase from 62 percent to 91 percent for cooling tower blowdown and from 29 percent to 50 percent for the ash pond effluent. However, nickel, vanadium, arsenic and

TABLE 6-7. PLANT 5604: INORGANIC REMOVAL EFFICIENCIES FOR LIME PLUS FERROUS SULFATE PRECIPITATION
(Concentrations in ppb unless otherwise noted)

	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Arsenic	7	<1[a]	>86	<1	<1	--
Antimony	5	5	0	6	30	--
Beryllium	<0.5	<0.5	--	2.5	<0.5	>80
Cadmium	<0.5	<0.5	--	1	<0.5	>50
Chromium	<2	<2	--	4	<2	>50
Copper	180	26	86	80	23	71
Lead	<3	<3	--	<3	<3	--
Mercury	<0.2	<0.2	--	<0.2	<0.2	--
Nickel	6	3	50	9.5	<0.5	>95
Selenium	<2	<2	--	3	3	0
Silver	3	10	--	5.5	5	9
Thallium	<1	<1	--	<1	<1	--
Vanadium	24	41	--	27	15	44
Zinc	780	36	95	300	25	92
Total Organic Carbon[b]	<20			<20		

[a] < - Designates concentration below detection limit.

[b] Values are in ppm.

TABLE 6-8. PLANT 1226: INORGANIC REMOVAL EFFICIENCIES FOR LIME PLUS FERROUS SULFATE PRECIPITATION
(Concentrations in ppb unless otherwise noted)

	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Arsenic	4	3	25	9	3	67
Antimony	7	9	--	7	9	--
Beryllium	<0.5[a]	<0.5	--	<0.5	<0.5	--
Cadmium	1.8	1.6	11	2.0	3.2	--
Chromium	5	3	40	6	4	33
Copper	47	<4	>91	14	7	50
Lead	3	<3	>0	4	<3	>25
Mercury	0.2	<0.2	>0	<0.2	0.6	--
Nickel	6.0	6.0	0	5.5	9.0	--
Selenium	<2	<2	--	8	7	13
Silver	0.7	0.4	43	0.5	0.4	20
Thallium	<1	<1	--	<1	<1	--
Vanadium	27	12	56	78	82	--
Zinc	26	2	92	7	6	14
Total Organic Carbon[b]	<20	<20		<20	<20	

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[a] < - Designates concentration below detection limit.

[b] Values are in ppm.

TABLE 6-9. PLANT 5409: INORGANIC REMOVAL EFFICIENCIES FOR LIME PLUS FERROUS SULFATE PRECIPITATION
(Concentrations in ppb unless otherwise noted)

	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Arsenic	<1[a]	<1	--			
Antimony	<1	<1	--	74	<1	>99
Beryllium	3.4	<0.5	>85	5	4	20
Cadmium	0.8	<0.5	>38	<0.5	<0.5	--
Chromium	37	<2	>95	<0.5	<0.5	--
Copper	620	48	92	<2	<2	--
Lead	70	<3	>96	26	18	31
Mercury	0.5	<0.2	>60	<3	<3	--
Nickel	4.0	3.6	10	<0.2	<0.2	--
Selenium	<2	<2	--	2.5	2.0	20
Silver	14	1.0	93	42	32	24
Thallium	8	<1	>88	1	1.1	--
Vanadium	11	46	--	9	7	22
Zinc	61	<2	>97	31	19	39
Total Organic Carbon[b]	21			11	<2	>82
				<20		

[a] < - Designates concentration below detection limit.

[b] Values are in ppm.

zinc all exhibited lower degrees of removal with ferrous sulfate added to lime. As most of the concentrations were very low, definitive conclusions cannot be made from the data.

A comparison of Tables 6-6 and 6-9 (Plant 5409) shows that, in most cases, the combination of lime and ferrous sulfate had equivalent or higher apparent removal efficiencies than lime alone. For instance, the apparent removal of silver from cooling tower blowdown was more than doubled, from 44 percent to 93 percent, by using both lime and ferrous sulfate as opposed to lime only. Although the removal effect of this chemical combination on other trace elements was not nearly so dramatic, the resulting removal efficiencies were higher. The only two exceptions were copper in the ash pond effluent and nickel in the cooling tower blowdown, both of which registered lower removal efficiencies for lime and ferrous sulfate. The apparent increase in the concentration for vanadium in the cooling tower blowdown was traced to contaminated filter paper.

6.2.3 Lime Plus Ferric Sulfate Precipitation

Ferric sulfate was added to lime to evaluate the effectiveness of this combination in removing arsenic and chromium. In these cases only arsenic and chromium were evaluated in the effluent. For Plant 5604, the reduction in arsenic was similar for both lime and lime plus ferric sulfate. Due to the low concentrations of arsenic and chromium in the influent streams, it was not possible to evaluate ferric sulfate performance.

For Plant 1226, arsenic removal was not higher with the combination than for lime alone. The arsenic concentration in the inlet was low for both cooling tower blowdown (4 ppb) and ash pond effluent (9 ppb). Chromium was reduced to the detection limit (2 ppb) for the ferric sulfate tests, while no removal was observed for lime alone. As in the case of arsenic, the inlet concentrations of chromium were very low, 4 ppb in the cooling tower blowdown and 6 ppb in the ash pond effluent.

At Plant 5409, ferric sulfate reduced the concentrations of arsenic and chromium to their respective detection limits (1.0 ppb and 2.0 ppb). This was an improvement over lime only for the case of chromium in the cooling tower blowdown. Chromium in the ash pond effluent was below the detection limit. As a direct result, nothing conclusive can be said about the effectiveness of this chemical in this application.

6.2.4 Lime Plus Sodium Sulfide Precipitation

A study similar to the test with ferric sulfate was performed with sodium sulfide. This test was developed to examine removal enhancement for cadmium and mercury.

At Plant 5604, cadmium and mercury were reduced to less than their detection limits, 0.5 ppb and 0.2 ppb, respectively. However, the results were the same with lime alone. As the inlet concentrations of cadmium and mercury were very low, 1 ppb or less in all cases, it was impossible to evaluate the removal effectiveness of this chemical for these conditions.

At Plant 1226, the cadmium concentration was nearly reduced to the detection limit, 0.5 ppb, with sodium sulfide. In the case of lime only, the results were inconclusive as the measured outlet concentration was greater than the inlet concentration for the cooling tower blowdown. No removal using sodium sulfide was observed for the ash pond effluent. Mercury was at the detection limit for both inlet streams.

At Plant 5409, lime plus sodium sulfide was effective in reducing the concentrations of cadmium and mercury to the detection limits. However, the results were the same as with lime precipitation. As the inlet concentrations of the two metals were low, less than 1 ppb in all cases, it is impossible to say conclusively what effect sodium sulfide has on removal of these metals.

6.3 REVERSE OSMOSIS

A portable reverse osmosis (RO) unit was used for the evaluation of this technology at each of the test sites. The unit was operated at each sample site for approximately two hours to simulate continuous operation. During the first hour conductivity and pH measurements were made to determine steady state operation. Samples of the RO unit effluent were then taken during the second hour. Conductivity and pH measurements made during this sampling period indicated that, in general, there were no significant variations resulting from fluctuations in feed compositions. The only exception to this observation occurred while sampling the cooling tower blowdown at Plant 1226. The samples at this location were obtained during shock chlorination and the quality of the water did vary over the testing time period.

The unit was designed to operate at 200 psi and 50 percent rejection, producing a clean water stream and a concentrated reject stream at a rate of 0.28 gallons per minute for each stream. A hollow fiber polyamide membrane was used in the unit. As the membrane is sensitive to certain water conditions, such as those producing scaling, fouling or chemical attack, preliminary tests were made on the wastewater streams to determine the need for pretreatment. Tests were run with a Hach test kit and a fouling index kit supplied by the manufacturer of the unit. Measurements were made of pH, turbidity, fouling index, free chlorine, iron and copper as the membrane is sensitive to certain extreme conditions associated with these.

Since the unit was in actual operation for such a short time, the primary reason for the pretreatment tests was to give some basis for evaluating the applicability of this technology under actual operating conditions. The pretreatment tests were conducted at each sampling site; however, only one stream, the cooling tower blowdown at Plant 5409, required pretreatment. The suspended solids loading in this stream was high.

6.3.1 Organic Analysis

The results of the chemical analyses for organic compounds in the effluent (product) stream from the reverse osmosis unit are presented in Tables 6-10 through 6-12. As discussed in Section 5, the wastewater streams at all the plants studied were relatively free of any priority organics. In the vast majority of the cases where compounds were observed, the concentration levels were very low. Only a few compounds of interest were confirmed as present in the inlet streams by the GC-MC analyses. As a direct result of the low inlet concentrations, it was not possible to observe any significant pollutant removal by use of the reverse osmosis unit.

The results of the analysis for removal of organic compounds by reverse osmosis for Plant 5604, presented in Table 6-10, indicate little about the suitability of this technology. The cooling tower blowdown and the ash pond effluent were very nearly void of priority organics. Measurable concentrations of benzene and toluene were observed in both streams. Slight removal of

TABLE 6-10. PLANT 5604: REMOVAL OF ORGANIC COMPOUNDS BY REVERSE OSMOSIS (Concentration in ppb)[a]

Compounds	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Chloroform		<1[b]	--	<1√[c]		--
Benzene	<1√		--	2.0√	1.4	30
Toluene	23.5√	20.5	13	3.5√	2.8	20
Ethylbenzene		2.6	--	<1√	2.1	--
Phenol	2.4[d]	N/A[e]	--		N/A	--
Dimethyl phthalate[f]	*		--			
Diethyl phthalate	*		--		*	--
Fluoranthene	2.0	<1	>50			
Butyl benzyl phthalate		*	--			
Bis (2 ethylhexyl) phthalate or 1,2 benzanthracene or chrysene		*	--		*	--
3,4 Benzofluoranthene or 11,12 benzofluoranthene	4		>75			
Di-n-butyl phthalate	*	*	--		*	--
1,3 Dichlorobenzene		2.0	--			
1,2,4 Trichlorobenzene or Hexachlorobutadiene		<1	--			
γ BHC or δ BHC (benzenehexachloride)		<1	--			
α Endosulfan		<1	--			

[a] A blank in the table signifies that a compound was not identified as being present.

[b] < - Designates concentration below detection limit.

[c] √ - Indicates that presence of this compound was confirmed by GC-MS.

[d] Evaporated - redissolved residue.

[e] N/A - Not Analyzed.

[f] Phthalates cannot be quantified due to sample contamination.

toluene, 13 percent, was observed for the cooling tower blowdown stream. However, considering the possible errors in measuring such low concentrations, the inlet and outlet values are very nearly the same. Some removal of benzene and toluene was observed for the ash pond effluent tests, 30 percent and 20 percent, respectively. Again, given the very low concentration levels and the possible errors of measurement, these removal efficiencies do not support definitive conclusions.

The results of the analysis for Plant 1226 are presented in Table 6-11. The untreated cooling tower blowdown at this plant contained significant concentrations of bromoform and dibromochloromethane, 154 ppb and 59 ppb, respectively. Nearly complete removal of these compounds was observed in the outlet from the RO unit. Both were reduced to their detection limit or lower. The grab sample used to quantify the inlet conditions was taken during shock chlorination, while the outlet samples from the RO were taken considerably later. During the operating time period, the inlet concentration could have changed, resulting in actual inlet concentrations less than the values presented in the table. No other compounds were observed in any quantity for either wastewater source with the exception of bromodichloromethane in the cooling tower water. The bromodichloromethane was not identified as being present in the RO unit product stream.

The organic analyses for Plant 5409 are presented in Table 6-12. Removal of three compounds from the cooling tower blowdown and one compound in the ash pond effluent was observed. All concentrations of these compounds in the two inlet streams were less than 4 ppb. At these concentration levels, the differences between the measured inlet and outlet concentrations are within the error limits; however, removal was observed in each

TABLE 6-11. PLANT 1226: REMOVAL OF ORGANIC COMPOUNDS BY REVERSE OSMOSIS (Concentrations in ppb)[a]

Compounds	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Hexachlorocyclopentadiene		<1[b]	--	<1	<1	--
4-Chlorophenyl ether					1.0	--
4-Bromophenyl ether or α BHC					1.5	--
γ BHC or δ BHC (benzene-hexachloride)	<1		--		<1	--
Aldrin					<1	--
Chloroform	<1✓[c]	<1	--			
1,1,1 Trichloroethane		<1	--			
Bromodichloromethane	8.2✓		>88			
Trichloroethylene		<4	--		<4	--
Dibromochloromethane	58.5✓	<1	>98	<1✓	<1	--
Bromoform	154✓	<1	>99	<1✓	<1	--
Tetrachloroethylene	<2	<2	--	<2	<2	--
Benzene	3.8		>74			
Toluene				<1	<1	--
Ethylbenzene		<1	--		<1	--
Phenol	1.7	N/A[d]	--	2.0	N/A	--
Dimethyl phthalate[e]	*	*	--		*	--
Diethyl phthalate		*	--		*	--

TABLE 6-11.
(Cont.)

Compounds	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Fluoranthene		2.7	--			
Butyl benzyl phthalate		*	--		*	--
Bis (2 ethylhexyl) Phthalate or 1,2 Benzanthracene or Chrysene	*	*	--		*	--
Di-n-butyl phthalate	*	*	--	*	*	--

[a] A blank in the table signifies that a compound was not identified as being present.
[b] < - Designates concentration below detection limit.
[c] √ - Indicates that presence of this compound was confirmed by GC-MS.
[d] N/A - Not Analyzed.
[e] Phthalates cannot be quantified due to sample contamination.

TABLE 6-12. PLANT 5409: REMOVAL OF ORGANIC COMPOUNDS BY REVERSE OSMOSIS (Concentrations in ppb)[a]

Compounds	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
1,3 Dichlorobenzene	1.0	1.0	--			
Bis (2-Chloro-isopropyl) ether or Bis (2-chloroethyl) ether				1.2		>17[b]
Hexachlorocyclopentadiene	<1	<1	--			
4 Bromophenyl ether or α BHC	<1	<1	--			
γ BHC or δ BHC (benzene-hexachloride)		1.3	--	<1		--
Aldrin				<1		--
Heptachlor epoxide	<1		--			
α Endosulfan	<1		--			
Dieldrin or DDE	<1		--			
Endrin		<1	--	<1		--
DDT				<1		--
1,1 Dichloroethane					<1	--
Chloroform	2.4✓[c]	<1	>58	<1	<1	--
1,2 Dichloroethane					<1	--
Bromodichloromethane	2.6✓		>62			
Trichloroethylene	<4✓	<4	--			
Dibromochloromethane	<1✓		--			
Benzene	1.5✓	<1	>33	1.0✓	<1	--

TABLE 6-12.
(Cont.)

Compounds	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency, %
Toluene				<1✓	3.3	--
Ethylbenzene					1.8	--
Phenol	4.1	N/A[d]	--	4.1	N/A	--
Dimethyl phthalate[e]	*	*	--	*	*	--
Diethyl phthalate	*	*	--		*	--
Fluoranthene	1.0	<1	--			
Butyl benzyl phthalate	*	*	--			
Bis (2 ethylhexyl) phthalate _or_ 1,2 benzanthracene _or_ chrysene	*	*	--		*	--
Di-n-butyl phthalate	*	*	--	*	*	--

[a] A blank in the table signifies that a compound was not identified as being present.
[b] < - Designates concentration below detection limit.
[c] ✓ - Indicates that presence of this compound was confirmed by GC-MS.
[d] N/A - Not Analyzed.
[e] Phthalates cannot be quantified due to sample contamination.

case. Toluene, present in the ash pond water, was observed in higher concentrations after the RO treatment. Nonetheless, some removal was observed as can be seen for chloroform (58%), benzene (33%) and bromodichloromethane (62%).

6.3.2 Inorganic Analysis

The results of the chemical analyses of inorganic compounds in the product water streams of the reverse osmosis (RO) unit are presented in Tables 6-13 through 6-15. As opposed to the organic analyses where no important organic species were present, several of the important inorganic species were detected in the inlet stream. As a result, it was possible to address removal efficiencies for these compounds.

The results of the analysis for inorganics in the product stream of the RO unit at Plant 5604 are presented in Table 6-13. In general, copper, vanadium, and zinc were present in significant concentrations. The observed removal efficiencies for copper were 82 percent and 89 percent for cooling tower blowdown and ash pond effluent, respectively. For zinc removal, the RO unit was 99 percent effective for cooling tower blowdown and 82 percent effective for the ash pond effluent. The results for vanadium differed in magnitude; in the cooling tower blowdown test only an 8 percent reduction was observed, while for the ash pond effluent 81 percent of the vanadium was removed. It is not known why this large difference occurred. The other metals were below 10 ppb in the inlet water. The RO unit removed portions of a few of these metals. In a few cases, the measured outlet concentration was higher than the inlet. Of those, only the arsenic and lead concentrations in the cooling tower blowdown appeared significant. The cyanide concentration in the ash pond was significant (22 ppb). The RO unit reduced cyanide 82 percent.

TABLE 6-13. PLANT 5604: INORGANIC COMPOUND REMOVAL EFFICIENCIES FOR REVERSE OSMOSIS (Concentrations in ppb unless otherwise noted)[a]

	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Arsenic	7	49	--	<1	<1	--
Antimony	5	2	60	6	3	50
Beryllium	<0.5	<0.5	--	2.5	5	--
Cadmium	<0.5	2	--	1	<0.5	>50
Chromium	<2	2	--	4	<2	>50
Copper	180	32	82	80	9	89
Lead	<3	20	--	<3	<3	--
Mercury	<0.2	<0.2	--	<0.2	<0.2	--
Nickel	6	0.5	>92	9.5	<0.5	>95
Selenium	<2	<2	--	3	<2	>33
Silver	3	4	--	5.5	2	64
Thallium	<1	<1	--	<1	<1	--
Vanadium	24	22	8	27	5	81
Zinc	780	<2	>99	300	53	82
Total Organic Carbon[b]	<20			<20		
CN^-	3	6		22	4	82
pH	6.9			5.6		

[a] < - Designates concentration below detection limit.

[b] Values are in ppm.

The results of the analyses for inorganics in the product stream of the RO unit at Plant 1226 are presented in Table 6-14. Only copper, vanadium and zinc were present in the inlet water at levels higher than 10 ppb. For these compounds, the removal performance varied. Approximately 79 percent of the copper was removed from the cooling tower blowdown, while only 29 percent of the copper in the ash pond effluent was removed. The outlet concentration for vanadium from treatment of cooling tower blowdown was significantly higher than the inlet. This increase could have been caused by time variability of the concentration of vanadium during sampling. About 82 percent of the vanadium was removed from the ash pond effluent. Greater than 93 percent of the zinc was removed from the cooling tower blowdown, while a zinc reduction of greater than 71 percent was observed for the ash pond effluent. The inlet zinc concentration for the ash pond was only 7 ppb, however. The results for the other species varied from instances where some removal was observed to instances where higher effluent than inlet concentrations were observed. The observed inlet concentrations for these species were low.

The results of the analysis for inorganics in the product stream of the RO unit at Plant 5409 are presented in Table 6-15. Several species were present in both the cooling tower blowdown and ash pond effluent at this plant. Chromium, copper, lead, silver, vanadium and zinc were all present in the cooling tower water in concentrations above 10 ppb. Arsenic, copper, selenium, vanadium and zinc were present in the ash pond effluent in concentrations greater than 10 ppb. As at the other plants, the removal performance was not consistent. About 92-percent removal of copper was accomplished in the cooling tower blowdown test, while only 65-percent removal was observed for the ash pond effluent. The inlet concentrations for these water streams were different by an order of magnitude, however. This case

TABLE 6-14. PLANT 1226: INORGANIC COMPOUND REMOVAL EFFICIENCIES FOR REVERSE OSMOSIS (Concentrations in ppb unless otherwise noted)[a]

	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Arsenic	4	<1	>75	9	1	89
Antimony	7	10	--	7	<1	>86
Beryllium	<0.5	<0.5	--	<0.5	<0.5	--
Cadmium	1.8	2.5	--	2.0	1.3	35
Chromium	5	<2	>60	6	<2	>67
Copper	47	10	79	14	10	29
Lead	3	<3	>0	4	<3	>25
Mercury	0.2	0.3	50	<0.2	<0.2	--
Nickel	6.0	3.0	--	5.5	5.0	9
Selenium	<2	<2	14	8	2	75
Silver	0.7	0.6	--	0.5	<0.2	>60
Thallium	<1	<1	--	<1	<1	--
Vanadium	27	58	--	78	14	82
Zinc	26	<2	>93	7	<2	>71
Total Organic Carbon[b]	<20	<20		<20	<20	
CN⁻	5	1	80	<1	8	--
pH	6.8			9.1		

[a] < - Designates concentration below detection limit.

[b] Values are in ppm.

TABLE 6-15. PLANT 5409: INORGANIC COMPOUND REMOVAL EFFICIENCIES FOR REVERSE OSMOSIS (Concentrations in ppb unless otherwise noted)[a]

	Cooling tower blowdown			Ash pond effluent		
	Inlet	Outlet	Observed removal efficiency,%	Inlet	Outlet	Observed removal efficiency,%
Arsenic	<1	<1	--	74	<1	>99
Antimony	<1	<1	--	5	3	40
Beryllium	3.4	<0.5	>85	<0.5	<0.5	--
Cadmium	0.8	<0.5	>38	<0.5	<0.5	--
Chromium	37	<2	>95	<2	<2	--
Copper	620	51	92	26	9	65
Lead	70	<3	>96	<3	7	--
Mercury	0.5	<0.2	>60	<0.2	<0.2	--
Nickel	4.0	3.6	10	2.5	1.5	40
Selenium	<2	<2	--	42	6	86
Silver	14	1.1	92	1	1	0
Thallium	8	4	50	9	<1	>89
Vanadium	11	16	--	31	21	32
Zinc	61	<2	>97	11	<2	>82
Total Organic Carbon[b]	21	<20	>5	<20	<20	--
CN^-	5	24	--	13	10	23
pH	6.8			6.7		

[a] < - Designates concentration below detection limit.

[b] Values are in ppm.

illustrates the dependence of removal efficiency on inlet concentration levels. The RO unit had very little effect on vanadium, with a higher outlet than inlet concentration for the cooling tower and only a 32-percent vanadium removal for ash pond effluent being observed. The removal of zinc was greater than 97 percent and 82 percent for cooling tower blowdown and ash pond effluent, respectively. The most dramatic result of the RO tests was over 99 percent removal of arsenic from the ash pond effluent.

6.4 VAPOR COMPRESSION DISTILLATION

The evaluation of vapor compression distillation as a control technology was conducted on an operating unit at Plant 3009. The unit treated wastewater from sources throughout the plant. This included some waste flow from the cooling water system and ash pond.

The primary intent of this evaluation was to determine secondary emissions of priority pollutants from the VCD unit. The unit has three major liquid streams (inlet, product, and brine reject) and a gaseous vent stream. The three major liquid streams were analyzed for inorganics and organics, with both a solid and liquid phase analysis for the concentrated brine. Time limitations prevented use of the GC-MS analysis to positively identify compounds that were tentatively identifed by the GC. For this reason, the data are presented exactly as analyzed by the GC.

An attempt was made to sample the deaerator vent for volatile organic and inorganic compounds. The method used to sample for organics involved drawing a measured amount of vapor through a Tenax column to be analyzed for volatile organics.

Unfortunately, water vapor in the vent gas caused swelling of the Tenax resin, preventing passage of the gas so that analysis of volatile organics was not possible. The vent was also sampled with a gold amalgamation trap designed to trap mercury for analysis.

6.4.1 Organic Analysis

The results of the analysis for organic compounds in the three liquid streams of the VCD unit are presented in Table 6-16. The concentration levels measured by the GC were generally low. These data are presented only to demonstrate that organics were not present in significant concentrations, and therefore no conclusions about the effectiveness of this technology can be made.

6.4.2 Inorganic Analysis

The results of the analysis for trace inorganic species are presented in Table 6-17. The streams covered include the inlet, the product, and the brine reject. The brine reject was a two-phase solution containing a dense brine phase and a solid phase. The two phases were separated and analyzed.

The concentrations for beryllium, cadmium, mercury, selenium, and thallium were low in both the inlet and the product. The VCD unit served to reduce the concentrations of copper, arsenic, zinc, and vanadium.

TABLE 6-16. PLANT 3009: REMOVAL OF ORGANIC COMPOUNDS BY VAPOR COMPRESSION DISTILLATION (VCD)
(Concentrations in ppb)[a]

Compound	VCD Feed	VCD Product	VCD Brine
Dimethyl phthalate[b]	*		
Diethyl phthalate	*		
Bis (2 ethylhexyl) phthalate *or* 1,2 benzanthracene *or* chrysene	*		
Di-n-butyl phthalate	*	*	
Pentachlorophenol	<1[c]	<1	<1
Phenol	1.3	8.7	14.8
1,3 Dichlorobenzene		<1	
Hexachloroethane *or* 1,2 dichlorobenzene			<1
Bis (2-chloro-isopropyl) ether *or* *bis* (2-chloroethyl) ether			<1
1,2,4 Trichlorobenzene *or* hexachlorobutadiene	<1		
Hexachlorocyclopentadiene	<1	<1	<1
4 Bromophenyl ether *or* α BHC			<1
γ BHC or δ BHC (benzenehexachloride)	<1		<1
Heptachlor *or* β BHC	<1		<1
Aldrin	<1		
α Endosulfan	<1		

---

[a] A blank in the table signifies that a compound was not identified as being present.

[b] Phthalates cannot be quantified due to sample contamination.

[c] < - Designates concentration below detection limit.

TABLE 6-17. PLANT 3009: INORGANIC COMPOUND ANALYSIS OF WATER SAMPLES FROM THE VCD UNIT (data in ppb unless otherwise noted)[a]

	Sample stream concentrations			
	Inlet	Product	Brine liquid	Brine solid
Antimony	7	3	150	1,000
Arsenic	49	<1	96	15,000
Beryllium	<0.5	<0.5	4	110
Cadmium	<0.5	<0.5	470	1,000
Chromium	5	<1	<1	38,000
Copper	2,700	10	31,000	270,000
Lead	7	<3	1,600	8,400
Mercury	1.5	2	2	1
Nickel	2.5	1	690	680
Selenium	<2	<2	<2	<2
Silver	15	2	1,200	3,400
Thallium	<1	<1	2,000	1,000
Vanadium	1,000	590	680	11,000
Zinc	910	6	3,300	220,000
CN^-	24	1.9		
TOC (ppm)	29	<20		

[a] < - Designates concentration below detection limit.

The deaerator vent vapors were analyzed for mercury as explained earlier. The analysis of the trap contents produced a measured concentration of 27 ± 10 mg of mercury per liter of the gas entering the trap. As no accurate exhaust flow rates for the vent are available, the exact concentration and mass flow rate of mercury cannot be determined.

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APPENDIX

TEST PLANS AND ANALYTICAL PROCEDURES FOR THE EVALUATION OF WASTEWATER TREATMENT TECHNOLOGIES FOR THE STEAM-ELECTRIC POWER INDUSTRY

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1.0 PREFIELD TESTING, FIELD PROCEDURES, AND PROCESS DESCRIPTIONS FOR TREATMENT TECHNOLOGIES

1.1 INTRODUCTION

The objective of this program was to assess available treatment technologies for control of priority pollutants in wastewater streams from the electric utility industry. The treatment evaluation program outlined in this Appendix is designed to determine if the chosen treatment technologies will remove the priority pollutants identified in the wastewater streams. Four treatment technologies were selected for evaluation in the utility industry:

1) Chemical precipitation
2) Vapor compression distillation
3) Carbon adsorption
4) Reverse osmosis

The study was to screen the wastewater controls in field tests to determine if they reduced priority pollutants to acceptable levels in plant effluents. Therefore, the study was limited to a bench-scale analysis performed on actual waste streams in four power plants. Due to the bench-scale nature and very short run times of the evaluations, no design or cost data for full scale applications were developed.

The Appendix describes the test plans developed and the analytical procedures used to quantify the priority pollutants in the plant water streams. Descriptions of the four treatment technologies under investigation are presented. A description of the general approach used to determine the performance of the treatment technologies is also presented.

1.2 PROCEDURE

The approach used to evaluate the controls involved three steps. These steps are as follows:

1) Design and construction of bench-scale equipment for the treatment technologies

2) Development of a testing program and analytical procedures

3) Field testing of treatment technologies

The development of the bench-scale designs for the treatment systems involved review of available design information for activated carbon adsorption and chemical precipitation. Literature sources and commercial vendors of these systems were contacted to obtain information. The information collected focused on the problem of assessing the technologies for removal of pollutants at the anticipated low concentrations. This was especially important in the design of activated carbon columns. A standard approach to evaluating carbon adsorption involves the use of batch isotherms. This approach is not practical for waste streams with organics in the parts per billion (ppb) concentration range. Therefore, carbon columns were built using accepted design practices for removal of small quantities of organic materials to evaluate the performance of carbon adsorption. These were used to determine whether carbon adsorption could remove the priority organics in the very low levels of concentration expected in the study. However, an adequate assessment of the overall performance of carbon adsorption, such as determining breakthrough, was not provided due to the lack of sufficient time to collect the data.

The evaluation of chemical precipitation used a standard approach to determine settling rates and removal efficiencies for trace levels of the priority metals. Lime precipitation was evaluated with and without additives. Sulfide precipitation was also evaluated.

The evaluation of reverse osmosis (RO) was conducted using a bench-scale unit to determine the suitability of RO as a pretreatment step prior to the other treatment technologies. The ability of the RO unit to concentrate the pollutants in the reject stream was also evaluated.

The evaluation of vapor compresssion distillation (VCD) was performed on an installed and operating unit at a power plant. It was not considered practical to design or purchase a bench-scale unit with the same capabilities. The primary purpose for evaluating the VCD unit was to determine the priority pollutants in secondary emissions from the units.

1.3 CHEMICAL PRECIPITATION

The objective of this test plan was to provide data necessary to examine the feasibility of chemical precipitation for removing the following inorganic priority pollutants:

1) antimony
2) arsenic
3) beryllium
4) cadmium
5) chromium
6) copper
7) cyanide
8) lead
9) mercury
10) nickel
11) selenium
12) silver
13) thallium
14) zinc
15) vanadium

The effectiveness of the treatment for reducing total organic carbon (TOC) was also examined. The streams tested were:

1) cooling tower blowdown
2) ash pond effluent

Lime was the primary precipitating agent examined. Sodium sulfide was tested for its ability to reduce cadmium and mercury since these metals may not be removed by lime treatment alone. Addition of ferric and ferrous sulfate with lime was also tested to examine their effect upon metals removal due to coprecipitation mechanisms.

1.3.1 Sampling Strategy

Water samples were taken from cooling tower blowdown and ash pond effluent. The samples were analyzed for the priority pollutants. These samples represented the inlet condition to the treatment process. One sample from each stream was tested with lime as the precipitating agent. Duplicate samples from each stream were tested with lime, lime with ferric and ferrous sulfate and sodium sulfide.

The performance of chemical precipitation for pollutant removal was determined by analyzing the treated samples for residual concentrations of the pollutants being investigated, as well as TOC. Table A-1 summarizes the testing strategy.

1.3.2 Equipment

The equipment used for testing with chemical precipitation is listed in Table A-2.

TABLE A-1. SAMPLING STRATEGY FOR CHEMICAL PRECIPITATION

Operation	Number of Samples per Stream	Number of Elements Analyzed for	Notes
Lime precipitation	1	15	Complete analysis
Lime precipitation plus ferric sulfate	1	15	Complete analysis
Lime precipitation plus ferrous sulfate	1	2	Analysis for chromium and arsenic
Lime/sodium sulfate precipitation	1	2	Analysis for mercury and cadmium
Raw water analysis	1	15	Complete analysis

TABLE A-2. CHEMICAL PRECIPITATION EQUIPMENT LIST

- Jar test apparatus
- pH meter
- Graduated cylinder - 1 liter
- Filtering apparatus
- Filter paper, 43 Whatman
- Precipitating reagents
  - Lime
  - Sodium sulfide
- Coagulant aids
  - Ferric sulfate
  - Ferrous sulfate
  - Betz 1100 Floc
- Bottle of nitric acid - double distilled
- Magnetic stirrer
- Pipets

1.3.3 Test Procedure

1.3.3.1 Preliminary Lab Testing--

The objective of the controlled laboratory testing program was to evaluate different precipitating methods before actual field testing was begun. The methods were to be similar to techniques used in public or industrial wastewater treatment facilities. The precipitation methods were tested for effectiveness of removing trace metals from utility wastewater streams.

Water treatment by chemical precipitation depends upon the type of contaminants present, the type and dosage of coagulants and coagulant aids, and the chemical characteristics of the water, i.e., pH, temperature, ionic strength, etc. Impurity removal is accomplished by any of the following mechanisms:

1) Precipitation - the formation of insoluble species by chemical addition

2) Coprecipitation - the formation of a solid solution of two or more species of similar size, electrical charge, or crystal morphology

3) Inclusion - the physical entrapment of impurities within the precipitate during the precipitation process

4) Adsorption - the adsorption of ions by active sites on the surface of a precipitate

5) Coagulation - the formation of a flocculent mass by the aggregation of fine suspended precipitate particles

The purpose of coagulant aids is to remove impurities that are too small to be removed by gravity settling. A variety of coagulants and settling aids is available. The control of pH and the proper choice of precipitation aids are the major factors in a successful water treatment process.

Lime (CaO or $Ca(OH)_2$) and soda ash (Na_2CO_3), are the two most common additives used for basic pH control. With soda ash there is no increase in hardness for the treated water; however, an increased potential for corrosion is observed. Lime is less expensive and also has the advantages of forming precipitates of $CaCO_3$ and $CaSO_4$. Metal oxide formation is most efficient with the pH between 10.5 and 12.5. Lime was chosen as the pH control agent. The removal of metal species as xoides will be enhanced by coprecipitating them with $CaCO_3$ and $CaSO_4$.

Aluminum, ferric and ferrous salts are the most widely used coagulants. Alum, potassium aluminum sulfate, is the standard coagulant used in wastewater treatment. Effective coagulation for alum is in the pH range 5.5 to 8.0. Alum reacts with the natural alkalinity of the water to produce carbon dioxide. This increases the corrosiveness of the water, which is undesirable.

Iron salts, though more expensive, are very effective in color removal and can be applied over a wider pH range than alum. Copperas (ferrous sulfate) is normally added with lime to form a precipitate of ferric hydroxide. Ferrous sulfate has the advantage of reducing hexavalent chromium to trivalent chromium which can then be precipitated as the metal oxide.

Both ferric sulfate and ferric chloride are used as coagulants alone or with lime. The optimum pH range is wide, 4 to 9, and the flocs formed are quick-setting. Ferric chloride is more efficient; however, it must be handled with corrosion-resistant equipment.

Some metals will not form oxides or hydroxides that can be precipitated. Metal sulfides, usually generated with either sodium sulfide or hydrogen sulfide, are generally less soluble in basic solution than the corresponding oxide. Sulfide addition can aid in the removal of certain metals, such as lead, mercury, and cadmium. These precipitates can be coagulated with the lime precipitation method.

Impurities can be removed by adsorption at active sites of the precipitate. Polyelectrolytes are water-soluble, high-molecular weight polymers. In solution, polyelectrolytes disassociate forming large, highly charged ions. There are three types of polyelectrolytes available: negatively charged or anionic polyelectrolytes, positively charged or cationic, and those that form both positive and negative charges, which are erroneously called "nonionic." Polyelectrolytes, because of the large size, also increase the settling rate.

Precipitation Results of Artificial Wastewater Sample--

An artificial wastewater sample was prepared by adding standard amounts of arsenic, chromium, copper, nickel, selenium, and zinc. The prepared samples contained metal concentrations of 3 ppm. These levels allowed for rapid analysis by atomic absorption using standard flame techniques. Removal efficiencies were calculated by the formula:

$$\% \text{ Removal} = \frac{C_o - C_t}{C_o} \times 100 \qquad (1\text{-}1)$$

where C_t is concentration of treated water and C_o is concentration of the untreated water, both for a given compound.

Table A-3 presents the data for the effective removal of metals with changing pH. The pH was controlled by lime addition. Lime was the only precipitating agent used. As can be seen, As, Cu, Ni, and Zn are all effectively removed by lime alone. The pH does not have a significant effect. A slight removal of Cr is seen at the higher pH level. However, no significant removal is seen for Se.

TABLE A-3. REMOVAL BY LIME TREATMENT AT VARIOUS pH'S

Final pH	Removal Efficiency (%)					
	As	Cr	Cu	Ni	Se	Zn
10.8	88	3	99+	99+	<1	99+
11.9	90	7	99+	99+	<1	87
12.3	92	22	86	99+	9	45
12.4	95	18	88	99+	<1	82

Two iron salts were tested for the effect on lime removal efficiencies. Various amounts of ferric sulfate were added to the sample and, then, the pH was raised to 11.5 with lime. A fast settling floc of ferric hydroxide was formed. Results of the ferric sulfate tests are shown in Table A-4.

TABLE A-4. REMOVAL BY FERRIC SULFATE AND LIME PRECIPITATION

Ferric Sulfate Concentration	Final pH	Removal Efficiency (%)					
		As	Cr	Cu	Ni	Se	Zn
110	11.5	97	8	99+	99+	21	99+
260	11.4	98	11	99+	99+	29	99+
510	11.1	99+	13	99+	99+	27	99+
1100	8.7	99+	30	99+	99+	83	99+

The effect of ferric sulfate on the removal of As, Cu, Ni, and Zn was not significant. Chromium exhibited an increase in removal efficiency as the concentration of ferric sulfate increased, although the increased efficiency was not large.

Selenium was removed with better efficiency with ferric sulfate present than with lime alone. A high removal was seen with a high concentration of iron.

The concentrations of ferric sulfate used in the laboratory were found to be excessive. For field testing, the concentration was lowered to 10 ppm to be consistent with most large scale treatment processes.

Ferrous sulfate (copperas) is oxidized to ferric hydroxide at high pH. Ferrous sulfate can also reduce hexavalent chromium to trivalent chromium at a low pH. The metal oxide is precipitated with lime. Table A-5 shows the effect of varying pH and copperas concentrations on the removal of Cr, As, and Se. The initial pH of the sample was low enough to allow reduction of Cr^{+6} and Cr^{+3}. The removal of selenium with copperas was low, just as was found with ferric sulfate.

TABLE A-5. EFFECT OF FERROUS SULFATE ON LIME PRECIPITATION

Ferrous Sulfate (ppm)	Final pH	Removal Efficiency (%)		
		As	Cr	Se
100	12.0	98	66	24
120	11.5	98	81	10
250	12.0	98	91	13
260	11.5	99	91	24

Potassium aluminum sulfate (alum) was added to increase precipitation rate. Removal efficiencies of As, Cu, Ni, and Zn were the same as for lime alone. No major removal increase was observed for chromium and selenium. Table A-6 shows the removal with lime and alum.

TABLE A-6. REMOVAL BY ALUM AND LIME PRECIPITATION

Alum Concentration (ppm)	Final pH	Removal Efficiency (%)					
		As	Cr	Cu	Ni	Se	Zn
84	11.5	92	9	99+	99+	<1	88
160	11.0	91	9	99+	99+	4	86
570	11.1	92	17	99+	99+	21	94
1100	9.4	98	15	99+	99+	21	99+

Two techniques were employed to remove metals which do not form insoluble oxides or hydroxides. The samples were brought to a pH of 11.5 with lime. Sodium sulfide was added to one and carbon dioxide was bubbled through a second. The final pH of both was measured. The results of these two techniques are presented in Table A-7.

TABLE A-7. REMOVAL BY SODIUM SULFIDE, CARBON DIOXIDE AND LIME PRECIPITATION

Additive	Additive (ppm)	Final pH	Removal Efficiency (%)							
			As	Cd	Cr	Cu	Ni	Pb	Se	Zn
Sodium Sulfide	50	11.6	86	99+	20	99+	99+	64	21	62
CO_2	--	6.4[a]	89	59	16	73	33	99+	27	39

[a] Initial, pH = 11.5

A final experiment was performed using the various precipitating agents at the chosen pH of 11.5. As seen in Table A-8, ferric sulfate was the most effective agent for overall removal of the metals tested at the given pH. Ferric sulfate was effective for all but chromium.

TABLE A-8. COMPARISON OF PRECIPITATING AGENTS ON LIME PRECIPITATION

Additive	Additive Concentration (ppm)	Final pH	Removal Efficiency (%)				
			As	Cr	Cu	Pb	Se
Alum	130	11.4	98	18	99+	--	13
Ferric sulfate	530	11.1	99	17	99+	99+	24
Betz 1100	10	11.3	99	11	99+	65	17
Ferrous sulfate	250	11.3	99	87	99+	99+	24
No additive	--	11.9	87	22	96	68	<1

A recovery study was performed by analyzing the treated sample and the precipitate formed. The total metal found was compared to the amount added. Generally, the amount found was within the limits of experimental error of the amount of metal added. In the lime-alum system, more lead was found after treatment. This was probably due to contamination from the alum. The recovery results are shown in Table A-9.

TABLE A-9. RECOVERY STUDY OF PRECIPITATION TESTS

Additive	Final pH	Percent Recovered		
		Cr	Cu	Pb
Lime + alum	11.4	88	87	156
Lime + $Fe_2(SO_4)_3$	11.1	90	91	78
Lime + Betz 1100	11.3	94	69	59
Lime + $FeSO_4$	11.3	85	92	84
Lime	11.9	81	84	39

Precipitation Results of Cooling Tower Blowdown and Synthetic Ash Pond Effluent

A synthetic ash pond sample was prepared by equilibrating bottom ash with deionized water. There was no pH adjustment.

Analysis of the raw, as well as the treated sample, revealed that concentrations were below the determination limits of the analytical methods used. Removal efficiencies were not calculated.

A sample of cooling tower blowdown was obtained from a local gas-fired steam station. This plant adds dichromate to the system for corrosion control. The raw sample and the treated sample were analyzed for chromium, mercury, and selenium. As expected, chromium was the only metal found in large concentrations. Ferrous sulfate, as shown in the control testing, was effective inthe removal of the chromate. Table A-10 presents the data for the results of the precipitation tests on cooling tower blowdown and synthetic bottom ash samples.

Experimental Procedure--

Jar test experiments were performed to evaluate the effect of pH and various precipitating agents on trace metals removed from water. Water samples of known trace metal concentrations were prepared. A sample of cooling tower blowdown was obtained from a local steam station. Synthetic ash pond effluent was prepared by mixing a sample of bottom ash from a western steam station with deionized water. All of the samples were subjected to various preciptating tests for evalution.

Jar tests were performed to simulate the various stages of mixing and settling basin activity in water treatment. A Hach Floc Tester, Model 15057 (Figure A-1), was used for all jar test procedures. The test apparatus consisted of a 600-ml beaker, a dasher/mixer, and a low-speed magnetic stirrer. The four steps of the simulated treatment process were: chemical addition, flash mixing, flocculation, and settling.

TABLE A-10. RESULTS OF PRECIPITATION TESTS

COOLING TOWER BLOWDOWN

	Initial pH	Cr	Hg	Se
Raw Sample	6.5	4.2 ppm	1.4 ppm	< 0.5 ppb

Treatment	Final pH	Removal Efficiency (%)	
		Cr	Hg
Lime	11.5	< 5	8
Lime + $FeSO_4$	11.6	74	< 5
Lime + Alum	11.4	24	< 5
Lime + $Fe_2(SO_4)_3$	10.9	11	14
Lime + Na_2S	11.6	17	< 5

SYNTHETIC BOTTOM ASH

	Cr	Hg	Se
Raw Sample	< 0.2 ppm	< 0.5 ppm	< 0.5 ppb

All treated samples were below detection limits listed for raw sample.

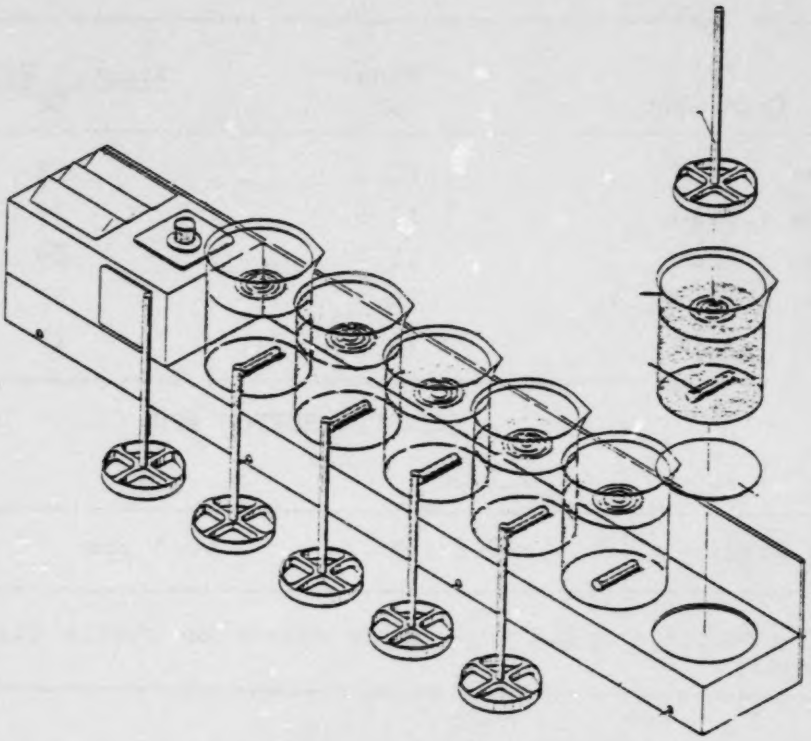

Figure A-1. Hach Floc Tester, Model 15057.

Jar Test Procedure--

A sample of water (100 to 500 ml) was placed in a 600-ml beaker. A magnetic stirring bar was placed in the sample and the beaker placed on the stirring base. The stirrer was turned on and the initial pH was then recorded. Aliquots of the pH control agents and coagulants were placed in the sections of the dasher/mixer. Flash mixing was simulated by quickly plunging and twirling the dasher/mixer in the sample. The stirrer timer was set for 30 minutes to allow for floc formation. The final pH was measured 20 minutes after flash mixing. Following flocculation, the stirring bar was removed and the sample was allowed to settle for 30 minutes. After settling, the sample was filtered and preserved for trace metal analysis.

A pH range of 9 to 13 was chosen because of optimum metal oxide formation in this range. Lime (calcium hydroxide) was chosen as the pH control agent. Coagulation and precipitation aids chosen were:

1) Potassium aluminum sulfate (alum)

2) Ferric sulfate

3) Ferrous sulfate (copperas)

4) Sodium sulfide

5) Carbon dioxide

6) Betz 1100

Preliminary testing for the optimization of the various parameters was conducted on the artificial wastewater sample of known trace metal concentration. Lime was used as the pH control agent as well as the main coagulant. Experiments were performed to measure the effect of the following on trace element removal:

1) pH
2) Alum addition
3) Ferric sulfate addition
4) Copperas addition
5) Sulfide addition
6) Carbon dioxide addition

The trace metals used in the preliminary testing were: copper, nickel, zinc, arsenic, selenium, and chromium. Copper, nickel, and zinc were chosen because of their typical transition metal behavior in oxide formations. Arsenic and selenium were chosen because of their amphoteric characteristics. Chromium was used because hexavalent chromium, or chromates, are used in corrosion control and present a problem to water treatment. Other elements used for certain tests were lead, cadmium, and mercury.

Treatment processes were applied to the cooling tower blowdown and ash pond liquor samples. Optimum conditions found in the previous experimentation were used to treat the samples.

Chemical precipitation, with the emphasis on lime precipitation, can be effective in the removal of most trace metals from utility wastewater streams. For plant design, an exhaustive test program needs to be performed using jar tests and analyses for individual plants and separate streams within the plant. Several factors are important in determining which precipitant and under what conditions the precipitation should be done. Each system will be different and require separate testing programs to predict the optimum operating parameters.

1.3.3.2 Field Testing--

Field testing of chemical precipitation proceeded as follows:

1) A 500-ml sample from the cooling tower blowdown and a 500-ml sample from the ash pond effluent were analyzed to determine priority pollutant concentrations, total suspended solids (TSS), total dissolved solids (TDS) and total organic carbon (TOC). In addition, five more 500-ml samples were taken from each of the two streams for precipitation testing.

2) Sample 1 from each stream was used to determine the quantity of lime which was needed to adjust 500-ml of that stream to a pH of 11.5. A pH meter and a calibrated pipet were used in a trial-and-error determination. The lime was taken from a 1-ℓ standard slurry solution of $Ca(OH)_2$ and deionized water. The quantity of lime slurry needed to adjust the sample to a pH = 11.5 was recorded.

3) Sample 2 was used to evaluate the effectiveness of lime precipitation. To this sample, the predetermined quantity of lime was added by flash mixing using the jar test apparatus. The sample was then slow-mixed on the tester for a 30-minute period. The solution was then filtered. Nitric acid was added to the filtrate to adjust the sample to a pH below 2.0 for preservation and sealed in a bottle for analysis later.

4) Sample 3 was used to determine the effect of ferric sulfate and lime on chromium and arsenic removal. Ten mg/ℓ of ferric sulfate, measured as iron, was first added to the sample by flash mixing using the jar test apparatus. Then, lime was added by flash mixing to adjust the pH to 11.5. After 30 minutes of slow mixing, the sample was filtered. The filtrate was adjusted to a pH below 2.0 using nitric acid and sealed in a bottle for analysis.

5) Sample 4 was used to examine the effect of ferrous sulfate as a coprecipitating agent with lime. The same procedure was followed for this sample as for Sample 3, substituting ferrous sulfate for ferric sulfate.

6) Sample 5 was used to investigate the effectiveness of using sodium sulfide

with lime to aid in removing cadmium and mercury. The same procedure was followed for this sample as for Sample 3, substituting sodium sulfide for ferric sulfate.

1.4 VAPOR COMPRESSION DISTILLATION

The purpose of this test plan was to examine the effectiveness of vapor compression distillation for utility wastewater cleanup. Sampling was done at a VCD unit in operation at a utility site. Samples were taken for trace metals, priority organic compounds, TDS, TSS, and TOC. Of prime concern was the distribution of the priority pollutants present in the feed between the product, vent, and brine streams.

1.4.1 Sampling Strategy

Grab samples of the feed, product, and waste streams were taken. The samples were preserved in the field as indicated in Table A-11. The samples were transported to and analyzed in the Radian Laboratory. The deaerator vent was sampled using appropriate sampling techniques. Mercury was collected using a gold amalgamation technique.

Organic samples from the vent were collected in a Tenax column. The Tenax sampling was done by taking measured gas samples in a gas-tight syringe. The gas was then purged through the Tenax resin column where the organics were trapped for later analysis with a gas chromatograph.

TABLE A-11. PRESERVATION TECHNIQUES FOR INORGANIC SAMPLES

Parameter[a]	Preservation	Container[b]
TDS, TSS		P, G
Metals	HNO_3, pH <2	P, G
Cyanide	Cool, 4°C NaOH, pH <12	P, G
TOC	Cool, 4°C H_2SO_4, pH <2	P, G

[a] TDS = total dissolved solids
TSS = total suspended solids
TOC = total organic carbon

[b] P = plastic, G = glass

Figure A-2 illustrates where the respective samples were taken at the VCD unit.

1.4.2 Equipment

The equipment used for sampling a VCD unit is listed in Table A-12.

TABLE A-12. VCD SAMPLING EQUIPMENT LIST

Pump	Tenax columns	Assorted bottles
Au amalgamation tube	Gas syringe	and glassware

1.5 ACTIVATED CARBON

A procedure for obtaining the data necessary to evaluate the feasibility of removing organics from utility wastewater streams by activated carbon is outlined. Two streams were examined: cooling tower blowdown and ash pond effluent.

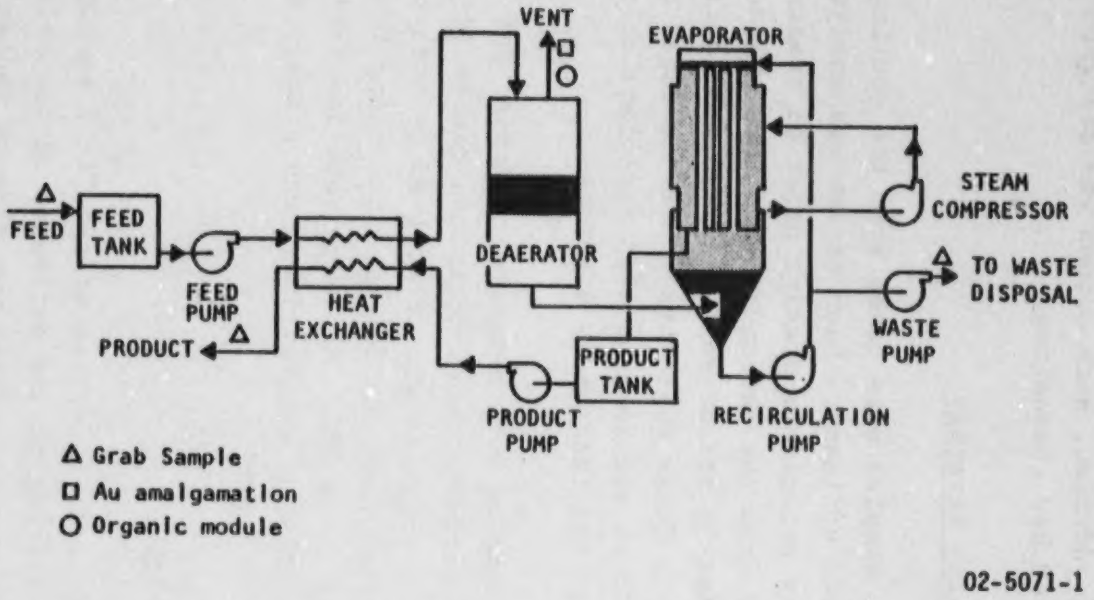

Figure A-2. Simplified system schematic of a brine concentrator.

In each case, activated carbon columns were operated on-site to simulate actual conditions for a large scale industrial activated carbon unit. Each column was carefully pretreated to protect against trace contamination resulting from carbon ash. In addition, each column was designed and operated to prevent packed bed channeling.

1.5.1 Sampling Strategy

Water samples were taken from the cooling tower blowdown and ash pond effluent. Each stream was analyzed for the organic priority pollutants present prior to treatment. Samples of the effluent from the carbon columns were collected and preserved appropriately for organic analysis. Volatile organics were preserved in Tenax resin traps. Extractable organics were preserved at 4°C as raw samples with methylene chloride and extracted later in the laboratory at Radian.

All samples were returned to Radian for a complete analysis. The performance of activated carbon for removal of organic priority organics was determined by analyzing the samples for concentrations of the compounds being investigated, as well as TSS, TDS, and TOC. Although some heavy metals removal has been noted in some applications, the primary emphasis on analysis was for organics.

1.5.2 Equipment

Table A-13 is a list of the field equipment necessary for the field testing of the activated carbon column. Carbon preparation and column packing was done at Radian's Austin Laboratories. According to an ash analysis provided by Calgon Corporation, Filtra-sorb 400 has slight traces of metallic oxides which can be partially removed by an acid wash. Therefore, before packing, the granular carbon was washed with a dilute nitric acid solution and then rinsed thoroughly twice with deionized water. The glass columns were also washed in this fashion. The columns were filled with carbon to a specified height to achieve a desired residence time. Each column was fitted with glass wool at both ends to prevent any shift in the carbon. The columns were transported to the field dry. In the field, deionized water was pumped through each column to afford deaeration and settling of the carbon. The carbon columns were then ready for use in sample treatment.

A Buchler peristaltic pump was used to regulate flow through the carbon columns. Other equipment used included a nitrogen purge apparatus and assorted glassware (for sample handling and preparation), Tenax resin traps (for volatile organic stabilization), methylene chloride (for liquid sample stabilization), and ice chests (for sample storage and shipment).

TABLE A-13. ACTIVATED CARBON FIELD EQUIPMENT LIST

Calgon Filtrasorb 400 Granular Activated Carbon	
Bulk Density	0.4 g/cc
Particle Density (wetted in water)	1.3-1.4 g/cc
Pore Volume	0.94 g/cc
Mean Particle Diameter	1.0 mm
Glass Column: 1.3-cm ID and 130 cm of carbon (15 min residence time)	
Buchler Peristaltic Pump (12 ml/min maximum flow)	
Miscellaneous	
Tenax-GC columns	Methylene chloride
Nitrogen purge apparatus	Ice chests

1.5.3 Test Procedure

The following test procedure for each stream and column was used to obtain the data necessary to evaluate the feasibility of removing organic substances from utility wastewater streams by carbon adsorption:

1) Before any on-site carbon testing was started, the column was set in a vertical operating position and loaded with deionized water. The purpose of this loading was to displace all the air in the column, as trapped air may cause channeling or bubbling and give erroneous results. The deaeration period was at least 24 hours. This period can be shortened somewhat by pumping deionized water through the column and by lightly tapping the sides of the column to dislodge trapped air bubbles.

2) After the column had been purged of entrained air, sample water from the streams to be tested was supplied to it. A four-gallon sample was sufficient for a six-hour operating supply for the carbon column.

3) A flow rate of about 10 ml/min was pumped through the column as each column was designed for a surface loading of approximately 8 $ml/min\text{-}cm^2$ ($2.0\ gpm/ft^2$).

4) Each column required a certain period of time to achieve stabilized operation. This period should be no less than four times the designed residence time for that column. For instance, a column designed for a 15-minute residence time will require an hour line-out period. After the line-out period, samples of the column effluent were collected for organic and trace element analysis.

1.6 REVERSE OSMOSIS

Reverse osmosis was identified as a potential pretreatment technology for the removal of all priority pollutants from utility wastewater streams. This section outlines the procedure used for obtaining the data necessary to evaluate the feasibility of removing heavy metals and organics from utility wastewater streams by reverse osmosis. Two streams were examined: cooling tower blowdown and ash pond effluent.

In each case, a portable reverse osmosis unit was operated onsite for a specified length of time to simulate continuous operation of a large-scale industrial reverse osmosis unit. For each stream tested, different pretreatments were required in order to prevent damage to the polyamide membrane resulting from scaling, fouling, or chemical attack. Necessary pretreatments were determined by onsite analysis of the stream with a Hach DR-EL/2 Test Kit.

1.6.1 Sampling Strategy

Two three-liter samples were taken at each sampling point for each of the utility wastewater streams tested. Grab samples were taken at the following points:

1) Initial intake (prior to booster pump, any pretreatment units, and RO unit)

2) RO product (immediately after the RO unit)

Organic samples consisted of three-liter volumes which were stabilized with 100 ml of methylene chloride and kept on ice. In addition, three 25-ml aliquots of sample were purged with nitrogen and volatile organics were captured in three traps packed with a Tenax resin which preserves the chemical integrity of each compound. These traps were desorbed for volatile organic analyses by gas chromatography at Radian's laboratory. All organic samples were taken in specially prepared teflon-capped bottles and kept on ice.

Three sets of 500-ml inorganic samples were taken at each of the sample points. The stabilization technique for each sample was determined by the subsequent laboratory analysis. TOC samples were stabilized with sulfuric acid to a pH less than 2. Cyanide samples were preserved with sodium hydroxide to a pH greater than 12, and trace element samples were preserved with nitric acid to a pH less than 2. The performance of reverse osmosis for removal of priority pollutants was determined by analyzing all samples of concentrations of the compounds being investigated, as well as TSS, TDS, and TOC.

1.6.2 Equipment

Table A-14 is a list of the field equipment used for the field testing of reverse osmosis performance. The major piece of equipment was the portable reverse osmosis (RO)

TABLE A-14. REVERSE OSMOSIS FIELD EQUIPMENT LIST

Continental Model 3011 RO Unit (0.28 gpm; polyamide membrane)
Hach DR-EL/2 Test Kit
Continental Fouling Index Test Kit
pH Meter
Teel Model 1P777 Rotary Gear Pump (booster pump)
Portable Power Generator
Pretreatment Units
  Water softener (for calcium and magnesium removal)
  Carbon filter (for free chlorine removal)
  Sand filter (for suspended solids removal)
  Aggregate gravel filter (for colloidal particle removal)
  Potassium permanganate filter (for iron removal)
  Phosphate filter (for sodium sulfate stabilization)
  Acid and chemical feed pump (for pH adjustment and/or cationic flocculent addition)
Miscellaneous
  A3200-M DuPont permeator
  Teflon tubing and fittings
  Tenax-GC columns
  Nitrogen purge apparatus
  1-gallon amber glass bottles
  Methylene chloride
  Ice chests

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unit manufactured by Continental Water Conditioning Corporation. The RO unit was designed to operate at 200 psi and 50% rejection, producing a clean water stream and concentrated reject stream at a rate of 0.28 gpm. The DuPont polyamide membrane is sensitive to various water conditions as shown in Table A-15. This sensitivity required some preliminary water analysis with the Hach Test Kit and Continental Fouling Index Test Kit to determine whether any pretreatment systems were necessary. The individual

TABLE A-15. INLET SPECIFICATION FOR DUPONT POLYAMIDE MEMBRANE

pH	$4 \le \mathrm{pH} \le 11$
Maximum Temperature	95°F (35°C)
Jackson Turbidity Units	≤ 0.3
Fouling Index	≤ 3.0
Free Chlorine	≤ 0.1 ppm for $4 \le \mathrm{pH} \le 8$
	≤ 0.25 ppm for $8 < \mathrm{pH} \le 11$
Iron	≤ 3 ppm for $4 \le \mathrm{pH} \le 5.5$ and no oxygen
	≤ 0.5 ppm for $5.5 < \mathrm{pH} \le 6.5$ and 1-5 ppm oxygen
	< 0.05 ppm for $6.5 < \mathrm{pH} \le 11$ and 1-10 ppm oxygen
Copper	≤ 2 ppm for $4 \le \mathrm{pH} \le 6$
	≤ 0.02 ppm for $\mathrm{pH} = 7$
	≤ 0.0002 ppm for $\mathrm{pH} = 8$

pretreatment units were equipped with Eastman quick disconnect couplings and could be easily connected in any combination to provide proper water conditioning for the RO unit.

A small portable power generator was used for the RO unit (110 volt, 5.8 amps, 60 Hertz, single phase AC) when no on-site power outlets were readily available. The generator was also used to power a booster pump which was required to draw water from standing pools, such as the ash pond. Additional equipment included a spare DuPont hollow fiber membrane, teflon tubing and fittings (for necessary plumbing), Tenax-GC columns and assorted glassware (for sample handling and preparation), nitrogen purge apparatus (for volatile organic stabilization), methylene chloride (for liquid sample stabilization), and ice chests (for sample storage and shipment).

1.6.3 Test Procedure

The following test procedure was used for obtaining the data necessary to evaluate the feasibility of removing the priority pollutants from utility wastewater streams by reverse osmosis. An identical test plan was followed for synthetically prepared samples as a part of a laboratory prefield testing program.

1) On a sample of the stream to be tested, the Hach Test Kit and Continental Fouling Index Kit were used as a means of estimating the pH and the amount of iron, calcium, magnesium, copper, free chlorine, suspended solids and dissolved solids in the stream. These preliminary tests determined what pretreatment, if any, was necessary.

2) The pretreatment units were arranged in the proper sequence and connected to the RO unit.

3) A booster pump upstream of the RO unit and any pretreatment equipment was used when the water stream to be sampled came from a standing pool or low pressure line (<40 psi).

4) Once the proper alignment of booster pump, pretreatment systems and RO unit was established, the process was ready for operation. The booster pump was started and the RO intake pressure gauge was checked to be certain there was pressurized water feed to the system.

5) If the RO pump pressure failed to rise above 10-15 psi, the RO unit was shut off and the system was purged of any trapped air. Purging was accomplished by leaving the booster pump on and disconnecting the system inlet line immediately prior to the RO unit. When a steady stream of water flowed at the disconnected point, the pressurized water had forced the air from the system. If a booster pump was not in use, the valve to the sample line was left open and adequate water pressure (60-100 psi) was supplied to purge the air.

6) Once the RO unit was operating, the conductivity of the initial intake and RO product streams was checked. When the conductivity of the RO product reached 5-10% of the initial intake, the system was operating at typical steady state. The RO unit continued to operate for another 30 minutes and the conductivity was checked again to ensure steady state operation. At this time, two three-liter samples were taken at the following points:

   a) Initial intake (prior to booster pump, any pretreatment units, and RO unit)

   b) RO product (immediately after the RO unit)

2.0 ANALYTICAL PROCEDURE FOR ANALYSIS OF ORGANICS

There has been little investigation of trace pollutants in wastewater streams from electric utility power plants, particularly for organics. The technical approach for organic analysis in an investigation of wastewater streams at four representative U.S. coal-fired utility plants is described. These wastewater streams were sampled before and after four possible water treatment technologies and then analyzed for contaminating organic and inorganic priority pollutant species.

Based on preliminary data, organic compounds from the priority pollutant list were identified as the organic compounds of major concern in the Radian study. The compounds are presented in Table 3-2 of this report.

The organic analyses were conducted for both purgeable and extractable compounds using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The procedures used for each type of analysis were based on the analytical schemes devised by the U.S. Environmental Protection Agency in its protocol document, Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants (Reference A1). To optimize results, some alterations in the instrumentation and the laboratory procedures were made in accordance with recent information, particularly with respect to the gas chromatographic technique.

2.1 SAMPLE COLLECTION PROCEDURE FOR GC AND GC-MS ANALYTICAL METHODS

Preparation for sample collection and sample preservation was designed to circumvent, as much as possible, certain problems considered inherent to the type of analyses which were to be conducted. Extreme caution in the preparation of sampling equipment and the execution of sampling technique was required. Contamination of samples was a continual hazard due to sensitive analytical instrumentation employed and the range of concentrations for the compounds considered.

2.1.1 Bottle Preparation, Packing, and Shipment

The procedure for bottle preparation was devised, in part, based on the U.S. EPA protocol for the measurement of toxic substances (Reference A1). Cleaning reagents were changed to avoid the introduction of additional organic material as possible sources of contamination.

Samples for the analysis of volatile organics were taken in 40-ml glass vials with screw caps. These vials were washed with a 50% solution of nitric acid and rinsed several times with deionized water. They were baked for one hour in a muffle furnace at 300°C. The screw-type caps were washed, rinsed, and allowed to air dry. They were then lined with teflon cap-liners having adhesive backing. When the baked vials had cooled, they were tightly capped and packed.

The 1-gallon bottles used to store samples for the analysis of extractable organic compounds were likewise washed with a 50% solution of nitric acid and rinsed with deionized water. These bottles were then capped with teflon-lined screw-type caps and packed.

Cleaned, empty bottles were packed and transported in cardboard boxes by van or trailer to the sampling site. Upon sample collection and after preliminary sample preservation measures had been taken, three 1-gallon bottles were packed in each insulated cooler container which was lined with fitted foam rubber packing. Tenax resin traps of purged samples were also placed in these coolers along with duplicate sample-containing vials. The coolers were equipped with a sufficient number of reusable "Blue Ice" packs to refrigerate the samples at a temperature of 4°C or less, for a period of approximately two days. The samples were maintained in this refrigerated state during their transport by van to the Radian laboratories. Once they had arrived, the samples were either immediately analyzed or were kept refrigerated until the time of analysis.

2.1.2 Sampling Technique and Sample Preservation

The sampling procedure and means of sample preservation differed according to whether the sample was to be analyzed for volatile organics or for extractable organic compounds. The flow diagram presented in Figure A-3 outlines the sampling and sample preservation procedures used for purgeable and extractable samples.

The points at which water samples were taken to be analyzed for priority pollutants were from untreated water sources and after treatment of utility wastewater streams at coal-fired utility plants:

1) Untreated Water Sources

- Plant makeup water
- Cooling tower blowdown
- Ash pond effluent

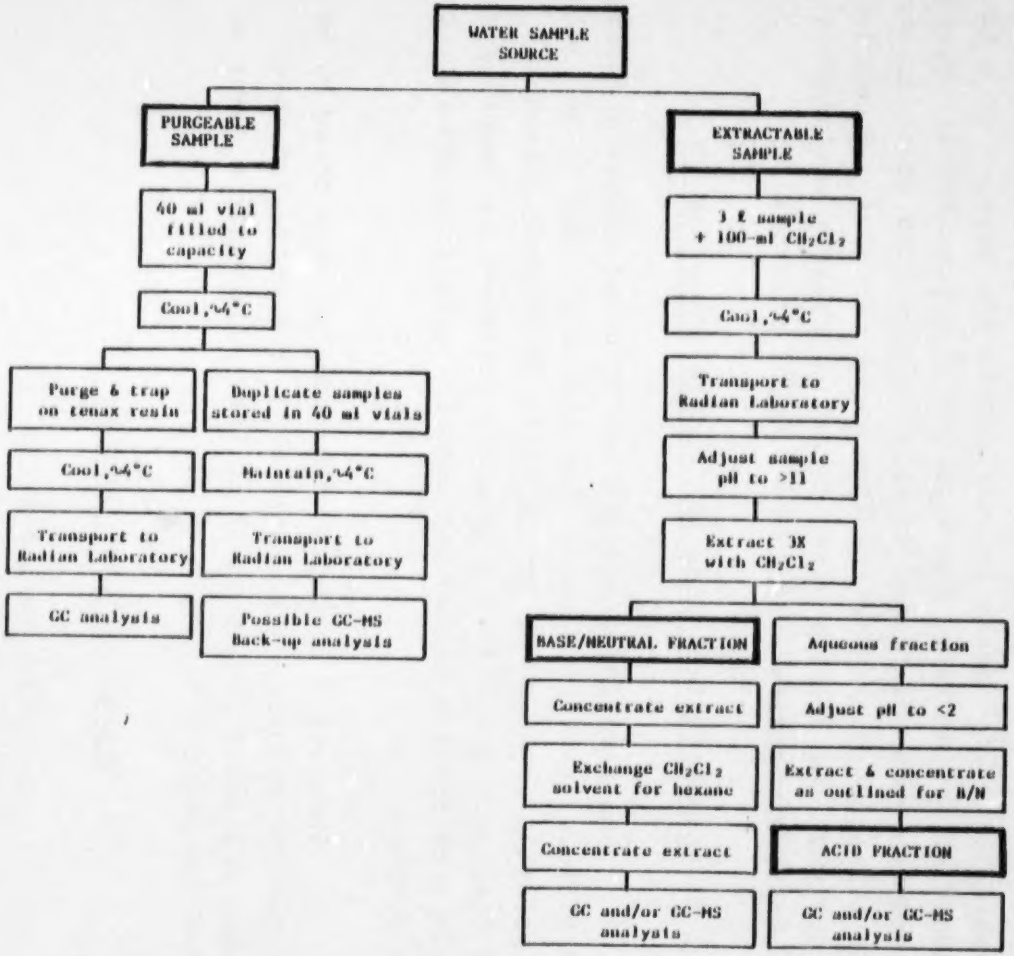
WATER SAMPLE SOURCE
PURGEABLE SAMPLE
40 ml vial filled to capacity
Cool, ∿4°C
Purge & trap on tenax resin
Cool, ∿4°C
Transport to Radian Laboratory
GC analysis
Duplicate samples stored in 40 ml vials
Maintain, ∿4°C
Transport to Radian Laboratory
Possible GC-MS Back-up analysis
EXTRACTABLE SAMPLE
3 ℓ sample + 100-ml CH2Cl2
Cool, ∿4°C
Transport to Radian Laboratory
Adjust sample pH to >11
Extract 3X with CH2Cl2
BASE/NEUTRAL FRACTION
Concentrate extract
Exchange CH2Cl2 solvent for hexane
Concentrate extract
GC and/or GC-MS analysis
Aqueous fraction
Adjust pH to <2
Extract & concentrate as outlined for B/N
ACID FRACTION
GC and/or GC-MS analysis

Figure A-3. An outline of field sampling procedure and sample preservation.

- Feed to a vapor compression distillation unit (VCD) (extractables, only)

2) Treated Water Sources

- Cooling tower blowdown after treatment by reverse osmosis
- Cooling tower blowdown after treatment by activated carbon
- Ash pond effluent after treatment by reverse osmosis
- Ash pond effluent after treatment by activated carbon
- Brine from a VCD unit (extractables, only)
- Product from a VCD unit (extractables, only)

Volatile Organic Compounds

The Bellar purge and trap method was closely followed for the analysis of volatile organic compounds. "On-site purging" was practiced for all samples to be analyzed by gas chromatography. Duplicate samples were taken and transported back to Radian in vials for possible GC-MS analysis.

The purgeable samples were obtained in 40-ml glass vials with teflon-lined screw-type caps. The vial was carefully filled from the appropriate water source without aeration or overfilling the bottle. Additional sample was added until the meniscus was visible above the lip of the vial. The cap was screwed on the vial in such a way as to leave no visible bubbles of air when the bottle was inverted. The samples were cooled to ∿4°C until they were purged onto a Tenax resin trap or were returned to the laboratory, still in the vial, to be purged and analyzed there.

The purge procedure involved purging a 25-ml aliquot of water sample, spiked with an internal standard, for 12 minutes with zero grade nitrogen gas at a rate of 40 ml/min. Purgeable organic compounds were evolved during the purge process and were trapped on a resin column. The column or "trap" used in each case was a 10-in. long, 1/16-in. ID, glass-lined stainless steel tube. Each column was packed 2:1 with Tenax resin and silica gel, respectively. The packing was held in place by cleaned glass wool at both ends of the column. Newly packed traps were baked for one hour in an oven set at 200°C and then sealed with Swagelok caps before they were transported to the field.

In the field, standard solutions comprised of the volatile organic compounds of interest were purged with each set of samples. After the samples and standards were collected on the resin traps, they were refrigerated at ∿4°C and maintained at that temperature until the time of GC analysis.

The practice of on-site purging was considered to be advantageous from a logistical as well as an accuracy standpoint. The on-site purging method insured immediate sample preservation, as accurate a collection of volatile organics as possible, and a safe and expedient means of shipment with reduced risk of sample bottle breakage.

Extractable Organic Compounds--

The extractable samples were stored in 1-gallon amber glass bottles containing 100-ml of methylene chloride, "distilled in glass." Three liters of a water sample were measured and emptied into the sample bottles. The bottle was sealed tightly and shaken vigorously to afford adequate mixing of the organic and aqueous layers. All samples were then cooled to ~4°C and maintained at that temperature until the extraction procedure could be completed at the Radian laboratories.

The sample extraction procedure used was a preliminary step in the extraction and separation of organic compounds. Two generalized extraction fractions were obtained for any given sample:

1) Base/neutral compounds extracted first, according to the procedural outline

2) Acidic compounds

The extractable samples were typically three liters plus the 100-ml methylene chloride preservation additive. A sample was first adjusted, while still in the sample bottle, to a pH of 11 or greater with 6N sodium hydroxide. An internal standard of hexachlorobenzene was added at this point. The gallon bottle was resealed and shaken to suspend any sediment. The sample was measured into a graduated cylinder and poured into a four-liter separatory funnel. The initial volume of the methylene chloride solvent was adjusted to 300 ml. The separatory funnel was shaken for two minutes or until an emulsion was broken.

The organic layer was then separated from the aqueous layer. Two more solvent additions of 150 ml each were made to the aqueous fraction and, once extracted, were combined with the first of the organic extractions. This combined organic fraction contained ~66% of the basic and neutral components of the raw sample. The base/neutral fraction was dried over previously extracted and cleaned sodium sulfate and reduced to a volume of <10 ml. The solvent was changed to hexane, and further concentration with a micro-Snyder column was carried out to a final sample volume of 1.0 ml. The sample was then ready for base/neutral analysis by GC and/or GC-MS.

The aqueous layer in the separatory funnel was acidified to a pH of less than 2 with 6N hydrochloric acid. The extraction and concentration steps for the acid fraction were performed in the same manner used to obtain the base/neutral fraction.

2.1.3 Discussion

Potential sources of sample contamination, at least in part, have been identified. Plastics of any kind which were used in the sampling and/or analytical procedures were suspected of contaminating samples through the leaching of plasticizer phthalates, e.g., di-n-butylphthalate and bis(2-ethylhexyl) phthalate. Contamination of samples also could have occurred using glassware that retained residual amounts of cleaning solvents on the glass surface, e.g., methylene chloride. Precautions were taken to minimize these effects.

As was mentioned earlier, the extraction procedure followed was not a technique for the refined separation of even classes of compounds. Rather, several classes of organic compounds were extracted into one fraction, e.g., the base/neutral fraction which contained a long list of basic and neutral compounds (including pesticides and metabolites) that were either halogenated or non-halogenated, either aromatic or non-aromatic, possible combinations thereof, etc. Hence, analysis of such complex mixtures offered inevitable interferences since detection of only a few compounds at very low concentration levels was required.

Typically, these compounds that are considered priority pollutants comprised no more than ~5% of the total organic content in any given water sample. Approximately 80-90% of the remaining organics in natural waters consisted of humic and fulvic acids. Although these acid compounds are bulky, complex, and largely ionic molecules which do not lend themselves well to an extraction technique, they are in any case partially extracted. Both humic and fulvic acids were expected to present some degree of interference to a sensitive analytical technique such as gas chromatography.

Sources of contaminating interferences were related to the extraction procedure itself. All extraction fractions were filtered to remove residual moisture before they were concentrated. Schleicher and Schuell analytical filter papers were used for this purpose. An investigation of the extraction procedure revealed that contamination of sample solutions resulted from these filter papers. Specifically, di-n-butylphthalate was identified as a contaminant from these papers. Possibly, there were other contaminating phthalates from this source as well.

In some instances, sample fractions were filtered twice. When sample fractions could not be concentrated on the same day that they were extracted, they were first filtered and then refrigerated. Condensate formed in the bottles during the period of refrigeration so the samples were refiltered to remove the additional moisture before the concentration procedure was initiated. Double filtering afforded more contamination potential than otherwise would have been expected.

2.2 METHODS OF ANALYSIS FOR ORGANIC COMPOUNDS

The technique of gas chromatography-mass spectrometry (GC-MS) was used as a back-up method to GC analysis for the positive identification of compounds comprising the raw inlet samples. Mass spectral analysis, according to the procedure outlined in the EPA Protocol (Reference A1), provided for comprehensive computer searches of samples for the programmed detection of any compound specified by the Consent Decree List of compounds.

The 129 "unambiguous priority organic pollutants" associated with the Consent Decree are categorized into two groups, dependent on the type of sample preparation required for their analysis:

1) Purgeables - those organic compounds that are amenable to the purge and trap method and subsequent analysis by gas chromatography

2) Extractables - those organic compounds that are solvent extractable and amenable to gas chromatography

2.2.1 Organic Analysis by Gas Chromatography

Analysis of priority pollutants by gas chromatography can be applied to concentrations in the parts per billion range.

Only recently has there been concern for the presence of organics at these levels of concentration. Consequently, very few standards for regulation of organic concentration levels in water, natural or otherwise, have been officiated by the Government. Interim standards, such as exist now, have been applied to a few organic pesticides. These compounds are listed in Table A-16 (Reference A2).

Gas chromatography was used more extensively than GC-MS in the analysis of organics in water samples. Utility plant makeup water samples and all untreated and treated utility wastewater samples examined were analyzed by GC and its associated detector unit.

TABLE A-16. MAXIMUM CONTAMINANT LEVELS FOR ORGANIC CHEMICALS [a]

Contaminant	Level, milligrams per liter
A. Chlorinated Hydrocarbons	
Endrin (1,2,3,4,10, 10-hexachloro-6, 7-epoxy-1,4, 4a,5,6,7,8,8a-octahydro-1,4,-endo,endo-5, 8-dimethanonaphthalene).	0.0002
Lindane (1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer).	0.004
Methoxychlor (1,1,1-trichloro-2,2-bis[p-methoxyphenyl] ethane).	0.1
B. Chlorophenoxyls:	
2,4-D, (2,4-dichlorophenoxyacetic acid).	0.1
2,4,5-TP Silvex (2,4,5-trichlorophenoxypropionic acid).	0.01

[a] Source: Reference A2

Analysis was based on detection of any compounds reported as having been identified in trace amounts in some utility wastewaters or compounds commonly found in water samples. Table A-17 presents a list of these compounds organized according to the procedure and method of analysis, i.e., whether compounds are purgeable or extractable from water samples and whether their measurement employed a Hall or Flame Ionization Detector.

TABLE A-17. ORGANIC COMPOUNDS IDENTIFIED FOR GC ANALYSIS

PURGEABLES - HALL DETECTOR

Bromodichloromethane
Bromoform
Chloroform
Chloromethane
Dibromochloromethane
1,2-dichloroethane
Tetrachloroethylene
1,1,1-trichloroethane
Trichloroethylene
Trichlorofluoromethane

PURGEABLES - FLAME IONIZATION DETECTOR

Benzene
Ethylbenzene
Toluene

BASE/NEUTRAL EXTRACTABLES - HALL DETECTOR

Aldrin
γ-benzene hexachloride (or) δ-benzene hexachloride
2-chloronaphthalene
4-chlorophenyl ether
DDD (or) β-endosulfan
DDT
1,3-dichlorobenzene
1,4-dichlorobenzene
Dieldrin (or) DDE
α-endosulfan
Endosulfan sulfate (or) Endrin aldehyde
Endrin
Heptachlor (or) β-benzene hexachloride

BASE/NEUTRAL EXTRACTABLES - HALL DETECTOR (Cont'd)

Heptachlor epoxide
Hexachloroethane (or) 1,2-dichlorobenzene
Hexachlorocyclopentadiene
Methoxychlor
1,2,4-Trichlorobenzene (or) Hexachlorobutadiene

BASE/NEUTRAL EXTRACTABLES - FLAME IONIZATION DETECTOR

Acenaphthene
Acenaphthylene
1,2-benzanthracene (or) Chrysene (or) Bis(2-ethylhexyl) phthalate
3,4-benzofluoranthene (or) 11,12-benzofluoranthene
Butylbenzylphthalate
Diethylphthalate
Dimethylphthalate
Di-n-butylphthalate
Fluorene
Fluoranthene
Indeno (1,2;C,D) pyrene
Naphthalene
Phenanthrene (or) Anthracene
Pyrene

ACID EXTRACTABLES - HALL DETECTOR

Pentachlorophenol

ACID EXTRACTABLES - FLAME IONIZATION DETECTOR

Phenol

2.2.1.1 Instrumentation--

Water samples were analyzed using a Tracor 560 Dual Detector Gas Chromatograph equipped with the Flame Ionization Detector and the Tracor 700 Hall Electrolytic Conductivity Detector. The Radian-designed field purge unit (FPU) and desorption apparatus were employed for the volatile organic analysis (VOA) procedure. A Hewlett-Packard 3380A Data Integrator Recorder documented a visual display of the chromatographic data for every sample run and reported the GC retention time and integrated area of each recorded peak on the chromatogram.

2.2.1.1.1 Hall Electrolytic Conductivity Detector--The working concept of the Hall Electrolytic Conductivity Detector in GC Analysis is the selective detection of halogenated, nitrogenated, or sulfonated trace organic compounds. Such compounds that are contained in a sample solution are injected into a GC analytical column. As the compounds elute through the column in characteristic order and retention time, the column effluent is introduced into a high temperature pyrolyzer furnace consisting of a quartz reaction tube constantly fed by a reaction stream of hydrogen gas. The pyrolyzer converts specific elements in the organic compounds to soluble electrolytes. The electrolytes are combined with a stream of deionized liquid (ethanol) in a gas-liquid contactor. Those gaseous components, readily soluble and ionized in the liquid, are detected and measured by continuous monitoring of the electrical conductivity of the liquid via an AC bridge circuit and auxiliary integrator-recorder.

2.2.1.1.2 Flame Ionization Detector--The Flame Ionization Detector (FID) is considered to be a universal detector. However, there are a number of gases which give little or no signal when analyzed by the FID. Some of these compounds are therefore useful as solvents.

As with the Hall Detector, a sample is injected into a GC column and is eluted through the column. The organic compounds in the column effluent are burned by an oxidative hydrogen flame (fed with excess oxygen) to produce ionized molecular fragments. These ions are collected by means of an electrical field on a collector electrode. The individual compound response is monitored via an AC bridge circuit and auxiliary integrator-recorder.

2.2.1.1.3 Field Purge Unit (FPU)--An apparatus was devised at Radian Corporation that provided a simple and efficient means of purging VOA samples in the field. The Radian-designed portable FPU was used every time a VOA sample was to be purged whether it was under field conditions or at Radian Laboratories. The unit capacity for purging two samples simultaneously expedited the task of effecting sample preservation immediately following sample collection.

A minimal amount of equipment and space was needed for on-site purging of samples. Aside from the FPU itself, which contained all of the tubing and fittings required, there was an aspirator device equipped with vacuum pump. The aspirator was used for cleaning needles, syringes, and glassware. The needles and syringes were employed as a means of delivering samples and standards to the sample purge tubes. Extra purge tubes and other laboratory glassware were stocked in case of breakage. One tank of zero-grade nitrogen gas, used for purging samples on-site, sufficed for the entire sampling effort.

The portable purge unit was photographed in operation on-site and is shown in Figure A-4.

2.2.1.1.4 Desorption Device--An apparatus was constructed to be placed immediately over the in-port valve of the GC instrument for direct desorption of volatile compounds from the Tenax trap into the GC analytical column.

The desorption apparatus consisted of a cylindrically-shaped heating mantle attached to the vertical support by adjustable clamps. The inport valve to the GC column was modified in the case of the VOA to accommodate direct attachment of a VOA Tenax trap as its contents were analyzed. The mantle could be moved vertically such that it could be lowered to surround the Tenax trap, providing a heat-box effect. The mantle was then raised again for cooling and removal of the used trap. In the desorption mode, the Tenax trap was heated to 180-200°C and flushed with the nitrogen carrier gas. In this way, the desorbed volatile organics were loaded onto the front end of the GC analytical column and ready to be analyzed.

2.2.1.2 Instrument Operating Parameters--

Each of the sample fractions (1. purgeables; 2. base/neutral extractables; and 3. acid extractables) was analyzed by both the Hall and the F.I. detectors. The operating parameters of the GC and associated detectors varied depending on the type of sample fraction to be analyzed.

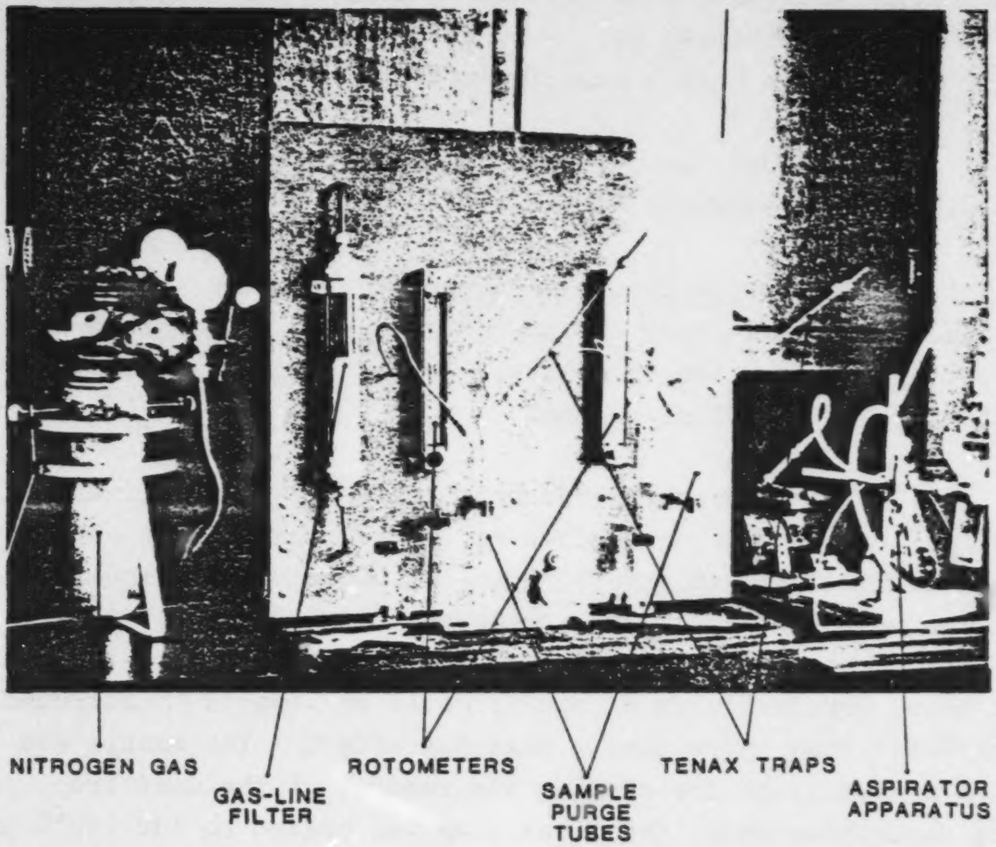

Figure A-4. Field purge unit (FPU).

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2.2.1.2.1 Purgeables--The same procedure for "purge and trap" was used for all purgeables analyzed by either detector. There were some variations, however, with respect to certain operating parameters of the analytical instrument assembly.

Hall Detector - The Tenax traps were heated rapidly to 180-200°C and back-flushed with zero-grade nitrogen gas at a flow rate of ~55 cm^3/min. The GC analytical column for the VOA procedure was a 6-mm OD, and 2-mm ID, nine-foot long coiled glass column. The first foot of the column was packed with 80/100 mesh Chromosorb coated with 3% Carbowax 1500. The remaining eight feet of the column were packed with 60/80 mesh Carbopac C coated with 0.2% Carbowax 1500. The GC oven was programmed for an initial temperature of 40°C. This temperature was held during the four-minute trap desorption period. At the end of this period, the oven was heated rapidly to 60°C and held at that temperature for four minutes. At this time, the oven was heated 8°C/min until it reached 170°C. The final temperature was held for 4-12 minutes to insure that all compounds had been eluted. The flow rate of the nitrogen carrier gas was ~55 cm^3/min. The flow rate of the zero-grade hydrogen reaction gas was ∿45 cm^3/min.

F.I. Detector - The Tenax traps were heated rapidly to 180-200°C and back-flushed with zero-grade nitrogen gas at a rate of 30 cm^3/min.

The GC analytical column used was the same as that used for the Hall Detector. The GC oven temperature program was the same as for the Hall Detector. The final temperature, however, was held for 10-15 minutes. The flow rate for the nitrogen carrier gas and for the hydrogen reaction gas was 30 cm^3/min. The flow rate for the zero-grade air was set at ~0.8 scfh @ STP.

2.2.1.2.2 Base/Neutral Extractables--The base/neutral (B/N) compounds were extracted in the first fraction obtained in the extraction procedure. Compounds classified as metabolites and pesticides were also extracted in this fraction. After the extracted fraction was concentrated according to procedure, it was ready for injection into the GC column and analysis.

Hall Detector - All of the B/N compounds were analyzed using a 6-mm OD, and 2-mm ID, six-foot long coiled glass column. The column was packed with six feet of 100/120 mesh Supelcoport coated with 1% SP-2250. The GC oven was programmed for an initial temperature of 50°C to be held four minutes. After four minutes, the temperature increased at a rate of 8°C/min until 260°C was reached. This final temperature was held 5-15 minutes. The carrier gas flow rate was ~55 cm^3/min. The hydrogen gas flow rate was set at ~45 cm^3/min.

F.I. Detector - The GC analysis parameters for the analytical column and the oven temperature program were the same as for the Hall detector.

However, the flow rates were somewhat altered for the carrier gas and the hydrogen gas, being ∿50 cm^3/min and ∿30 cm^3/min, respectively. The flow rate for the dry air was set at ∿0.8 scfh @ STP.

2.2.1.2.3 Acid Extractables--The acid extractables were obtained in the second fraction of the extraction procedure. One compound from this fraction was given particular regard and this was phenol. Although phenol was analyzed by FID, the acid fraction was also analyzed by the Hall Detector perchance some concentrated priority pollutant would be detectable.

Hall Detector - The GC column used to analyze the acid extractable compounds was the six-foot coiled glass column packed with six feet of 60/80 mesh Tenax GC. The GC oven temperature was programmed initially for 180°C (at the time of injection) and to progress at a rate of 8°C/min until 300°C was reached. This final temperature was held 10-15 minutes. The flow rates for the nitrogen carrier gas and the hydrogen reaction gas were ~55 cm^3/min and ~45 cm^3/min, respectively.

F.I. Detector - The Tenax GC analytical column was also used for the F.I. detection of acids. The Acid-Hall Detector program for the temperature regulation of the GC oven was used for F.I. analysis. The flow rates of the nitrogen carrier gas and hydrogen reaction gas were ∿50 cm^3/min and ∿30 cm^3/min, respectively. The dry air flow rate was set at ∿0.8 scfh @ STP.

2.2.1.3 Sample Analysis and Data Interpretation--

Identification and quantification by GC analysis of organic compounds in the three sample fractions (1. purgeables; 2. base/neutral extractables; and 3. acid extractables) were based on the percent recovery and relative retention time of internal standards (IS), i.e., measured aliquots of standard solutions of organic compounds used to spike the sample solutions. The internal standards used for the GC analysis were:

1) Purgeables - Hall Detector
   - 1,4-dichlorobutane (IS)
   - Bromochloromethane (IS)

2) Purgeables - F.I. Detector
   - Cyclohexane (IS)

3) Extractables - Both Hall and F.I. Detectors
   - Hexachlorobenzene (IS)

If an internal standard for some reason was not adequately recovered, straight retention times based on GC analysis of external standards were used to identify compounds. In such cases, quantification was calculated according to the percent recovery of an external standard which was analyzed on the same day as the samples being quantified. The external standards were those listed in Table A-16.

External standards were analyzed daily, with every 4-6 samples analyzed on one detector. This was done to insure sufficient monitoring of possible variation in the sensitivity of response and/or any other operating condition of the GC detector-recorder instrument assembly. Operating conditions as reflected by these standard runs provided the major source of information for understanding and interpreting the sample data.

Standard solutions were made up in concentrations commensurate with the concentration levels anticipated in sample solutions. For example, standards used in defining detection limit parameters were generally 4 ppb in concentration. In determining the detection limits, GC analyses of monitor-type standards were reviewed, taking into consideration ranges of percent recovery and relative retention times (RRT) and the background noise attributed to electrical noise and solution matrix. Realizing that sensitivity to GC analysis varied among the compounds being analyzed, standards for each compound were reviewed. A worst case response per compound was noted and a conservative detection limit was assigned in light of all identifiable interferences.

The variance in percent recovery was calculated from the high and low data points for each standard. Based on these figures, error limit approximations were calculated for all sample fractions analyzed by either detector unit:

1) Purgeables - Hall Detector

Detection Limit: 4 ppb, Trichloroethylene
2 ppb, Tetrachloroethylene
1 ppb, all others

Error Limit: ±30%, all compounds

2) Purgeables - F.I. Detector

Detection Limit: 1 ppb, all compounds
Error Limit: 50%, Benzene
20%, Toluene and Ethylbenzene

3) Base/Neutral Extractables - Hall Detector

Detection Limit: 1 ppb, all compounds
Error Limit: ±50%, all compounds

4) Base/Neutral Extractables - F.I. Detector

Detection Limit: 1 ppb, all compounds
Error Limit: ±50%, all compounds

5) Acid Extractables - Hall Detector

Detection Limit: 1 ppb, all compounds
Error Limit: ±50%, all compounds

6) Acid Extractables - F.I. Detector

Detection Limit: 1 ppb, all compounds
Error Limit: ±20%, all compounds

On several occasions, one or more peaks, discernible on a sample chromatogram, were not identifiable by the usual standards. In this event, a standard containing the full list of Consent Decree compounds corresponding to a given sample fraction (e.g., purgeables - Hall Detector) was analyzed for purposes of comparison (refer to Table A-18). If no identification could be made, the peaks were reported as "unidentifiable" and considered to be not representative of any priority pollutant as upheld by the Consent Decree.

In an effort to define a line of discrimination between spurious and 'discernible' peaks, three categories, A,

TABLE A-18. EPA CONSENT DECREE LIST OF "UNAMBIGUOUS PRIORITY POLLUTANT" ORGANIC COMPOUNDS

Purgeable Compounds	Extractable Compounds		
	Base/Neutrals	Pesticide & Metabolites	Acids
Chloroform	1,2,4-trichlorobenzene	4,4'-DDT	2,4,6-trichlorophenol
Bromoform	Hexachlorobenzene	4,4'-DDE	p-chloro-m-cresol
Bromodichloromethane	Hexachloroethane	4,4'-DDD	2-chlorophenol
Dibromochloromethane	Bis(chloromethyl) ether	Aldrin	2,4-dichlorophenol
Tetrachloroethylene	Bis(2-chloroethyl) ether	Dieldrin	Pentachlorophenol
Carbon tetrachloride	2-chloroethyl vinyl ether	α-endosulfan	2,4-dimethylphenol
Chlorobenzene	2-chloronaphthalene	β-endosulfan	Phenol
1,2-dichloroethane	1,2-dichlorobenzene	Endosulfan sulfate	2-nitrophenol
1,1,1-trichloroethane	1,3-dichlorobenzene	Endrin	4-nitrophenol
1,1-dichloroethane	1,4-dichlorobenzene	Endrin aldehyde	2,4-dinitrophenol
1,1,2-trichloroethane	4-chlorophenyl phenyl ether	Methoxychlor	4,6-dinitro-o-cresol
1,1,2,2-tetrachloroethane	4-bromophenyl phenyl ether	Heptachlor	
Chloroethane	Bis(2-chloroisopropyl) ether	Heptachlor Epoxide	
1,1-dichloroethylene	Bis(2-chloroethoxy) methane	α-BHC	
1,2-trans-dichloroethylene	Hexachlorobutadiene	β-BHC	
1,2-dichloropropane	Hexachlorocyclopentadiene	γ-BHC (lindane)	
1,3-dichloropropylene (cis and trans)	Acenaphthene	δ-BHC	
Methylene chloride	Fluoranthene	Toxaphene	
Chloromethane	Isophorone	Chlordane	
Bromomethane	Naphthalene	PCB-1242	
Trichlorofluoromethane	Bis(2-ethylhexyl) phthalate	PCB-1254	
Dichlorodifluoromethane	Butyl benzyl phthalate		
Trichloroethylene	Di-n-butyl phthalate		
Vinyl chloride	Diethyl phthalate		
Dichloroiodomethane	Dimethyl phthalate		
Acrolein	1,2-benzanthracene		
Benzene	benzo(a)pyrene		
Ethylbenzene	3,4-benzofluoranthene		
Toluene	11,12-benzofluoranthene		
Acrylonitrile	Chrysene		
	Acenaphthylene		
	Anthracene		
	1,2-benzoperylene		
	Fluorene		
	Phenanthrene		
	1,2:5,6-dibenzanthracene		
	Indeno(1,2:C,D)pyrene		
	Pyrene		
	Benzidine		
	3,3'-dichlorobenzidine		
	2,4-dinitrotoluene		
	2,6-dinitrotoluene		
	1,2-diphenylhydrazine		
	Nitrobenzene		
	N-nitrosodimethylamine		
	N-nitrosodipropylamine		
	N-nitrosodiphenylamine		

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B, and C, were described by which all of the possible peaks could be evaluated. To Category A were ascribed all spurious-type peaks which measured less than 2-3 times the height of the background noise. These were considered to be part of the background. Category B consisted of peaks which were definitely 'discernible' and which measured 4-5 times the height of the background noise. These peaks were equal to or greater than the detection limit for a given compound and were considered quantifiable. Category C consisted of peaks larger than those of Category A, yet measuring less than the detection limit, as defined. These peaks were considered 'discernible' and, if correspondent to identifying RRT's, were identified and reported as present in less than detection limit concentrations.

The occurrence of peaks considered either spurious or unidentifiable was principally attributed to the presence of other organics in the sample solutions. As stated earlier, the priority organics listed by the Consent Decree represent a very small percentage of the total organics in a water sample (refer to Section 2.3). The presence of other organics offered frequent interferences with the analysis of samples and with the interpretation of the data. Extraneous organics which were either inherent to a sample matrix or were the result of contamination may have:

1) Covered up or camouflaged other peaks which perhaps represented valid data

2) Prevented clean separation of peaks, hence, unresolvable peaks

3) Appeared at RRT's coincident to compounds of interest thereby causing false identification of compounds

4) Caused a large instrumental response interfering with normal base-line attenuation and obscuring the presence of pertinent compounds

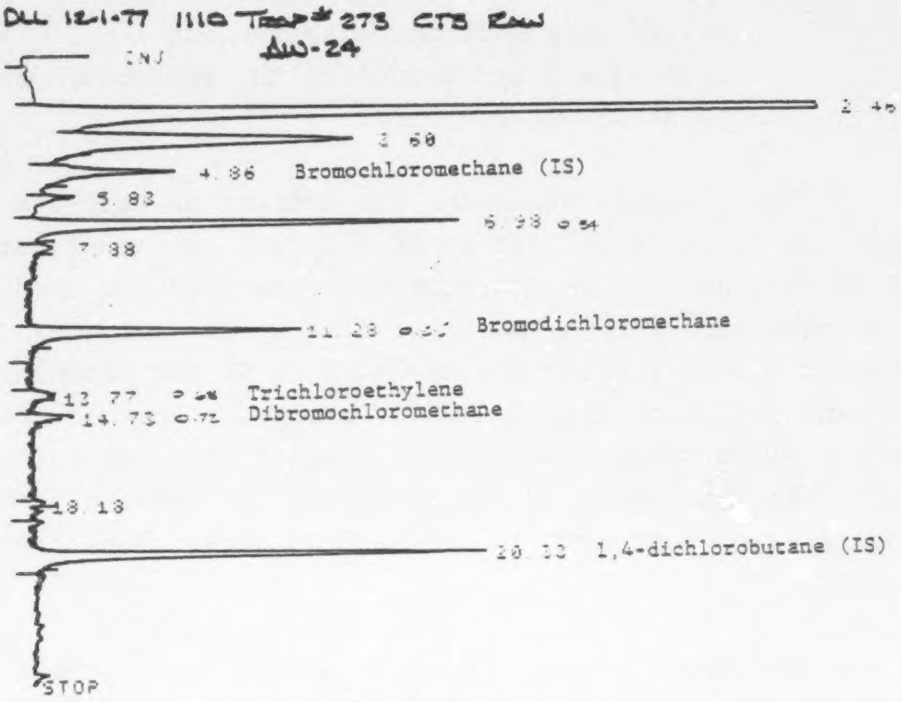
For a sample solution, the content of which is totally unknown, to be characterized by GC analysis, a back-up monitor by GC-MS instrumentation is required. The need for this practice is made apparent in the above discussion. However, it can be said of a sample solution, analyzed by GC for compounds of known sensitivity to this method of analysis, that if analysis shows no 'discernible' peaks to be present on a chromatogram at RRT's characteristic of the compounds of interest, then those compounds are not present in any amounts considered detectable by the GC.

An example chromatogram of a typical GC sample analysis is shown in Figure A-5. Compounds which were identified are indicated to the side of their identifying peaks along with their recorded retention times. Low background noise and good recovery of the internal standards (labeled) are demonstrated.

2.2.2 Mass-Spectral Analyses

The gas chromatography-mass spectrometry system (GC-MS) was used for confirmation of organic compounds detected by the GC analysis. GC-MS procedures followed the EPA Protocol as outlined in the EPA document, Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants (Reference A1).

All utility plant makeup water samples and all untreated wastewater samples were analyzed by the GC-MS. The GC-MS scope of analysis included the entire EPA Consent Decree List of organic compounds as shown in Table A-18.



RT	TYPE	AREA	AREA %	
2.45		1352839	53.13	
3.63	M	381583	14.99	
4.85	M	96498	3.79	
5.83		5881	.281	
6.98		257407	10.11	
7.88		12108	.475	
11.28		164244	6.451	
13.77		15249	.598	8
14.73		18495	.726	4
18.18		4442	.174	5
20.33		237432	9.325	

HP 3330A
DLY OFF STOP 30 REJECT 1000
MV/M 3.00 ATTN 32

Figure A-5. Example chromatogram of a typical GC sample analysis.

2.2.2.1 Instrumentation--

The water samples were analyzed utilizing a Hewlett-Packard 5982A combined Gas Chromatograph-Mass Spectrometer (GC-MS). A Hewlett-Packard 5834A Data System was used for the collection, storage and retrieval of data.

The GC-MS instrument consists of a Hewlett-Packard 5710A gas chromatograph and a Hewlett-Packard 5982A dodecapole mass spectrometer and GC-MS interfaces. The instrument is equipped with a dual ion source for operation in the electron impact or chemical ionization mode. The major features of the system include: 3-1,000 amu mass range covered in a single scale; adjustable scan rate of 325 amu/sec; sensitivity to picogram levels, even with large samples; provision for membrane and jet separators; analog to digital measurements at every 0.1 amu; and resolution permitting full separation of half masses.

The Hewlett-Packard 5933A data system controls the scan functions of the Hewlett-Packard mass spectrometer, and stores the acquired mass spectral data on magnetic discs. In addition, the Hewlett-Packard 5933A data system will search and compare acquired mass spectra against four disc-stored mass spectral libraries containing over 15,000 mass spectra. Radian also has the capability to access and search the data banks available from the Cyphernetics Corporation.

GC-MS system performance evaluation was conducted each day the system was used for these analyses, as it is for all samples analyzed by GC-MS at Radian. The computerized system was tuned and checked using decafluorotriphenylphosphine according to the recommended EPA procedure.

2.2.2.2 Sample Analysis and Data Interpretation--

Each of the sample fractions (1. purgeables, 2. base/neutral extractables, and 3. acid extractables) required a separate GC column for best resolution of the desired components. It was therefore necessary that three separate GC-MS runs be completed for each sample.

Three standard solutions were prepared to correspond with the three classes of organics being analyzed. These contained:

1) Purgeables in methanol solvent

2) Acid extractables in methylene chloride

3) Remaining compounds on the Consent Decree List also in methylene chloride solvent

These solutions were used to quantify the compounds found in the samples.

A typical qualitative analysis of a given sample was achieved by injection of a measured quantity of the material into the appropriate gas chromatographic column. Temperature programming was specific to the type of compounds being analyzed (purgeable or either extractable group) and the GC column being used. This was designed to maximize resolution of the organic compounds. As the organic species were eluted from the column, they were transferred to the ion source of the mass spectrometer through a membrane separator. The mass spectrometer was scanned continuously from a mass to charge (m/e) ratio of 50 to 450 with a cycle time of approximately 3 seconds. Electron impact (70eV) mass spectrometry was employed exclusively for the analyses. The mass spectra obtained were stored on a magnetic disc for future evaluation.

Qualitative identification of the compounds of interest was based on the appearance of key ions at specified m/e values and the correspondence with known gas chromatographic retention times for standards. In addition, each compound was positively identified only if the ratio of the intensities of the key ions for each peak corresponded to the intensity ratios for the standard mass spectra.

Quantitative analysis of the identified compounds was achieved through the selected ion monitoring (SIM) technique using the computerized mass spectral data. When resolution of the components of interest was not complete, selected ion fragments were chosen that were characteristic of the compound to be quantified. More than one ion fragment was selected in each case in order to maintain quality assurance and confidence that no significant ion counts were contributed by interfering peaks. Ratios of the ion counts of these fragments in the sample were compared to the same ratios in the standard.

For each compound, the area under the most abundant key ion was calculated using the data system. This computed area was compared to the areas found from analyzing standard mixtures, and the concentration of each compound in the sample was then determined by reference to a calibration curve.

Figure A-6 is a computer printout sheet depicting the GC-MS analysis for volatile organics in a utility wastewater stream. In this water sample, four halogenated volatiles were

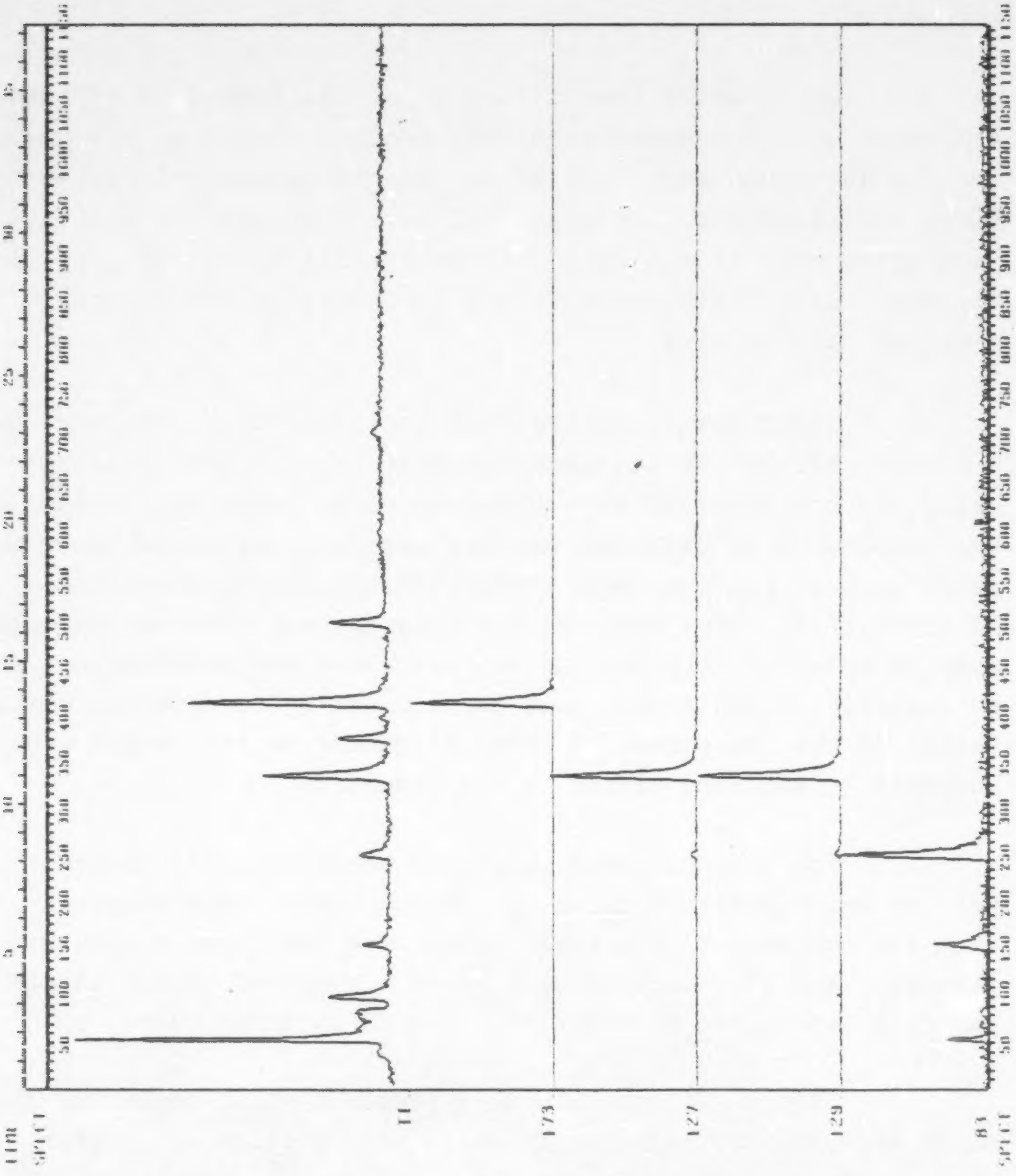


Figure A-6. Computerized printout of a mass spectral search for purgeable organics in a wastewater sample.

positively identified. The top line of the printout is a GC chromatogram representing total ion compositions (TI) of the compounds present. Each of the four lower lines represents a selected key ion fragment (Nos. 83, 129, 127, 173). Each of these key ions is characteristic of one or more compound. A combination of two or three (or more) key ions is usually a positive identifying feature of a given compound. The compounds identified in this sample were:

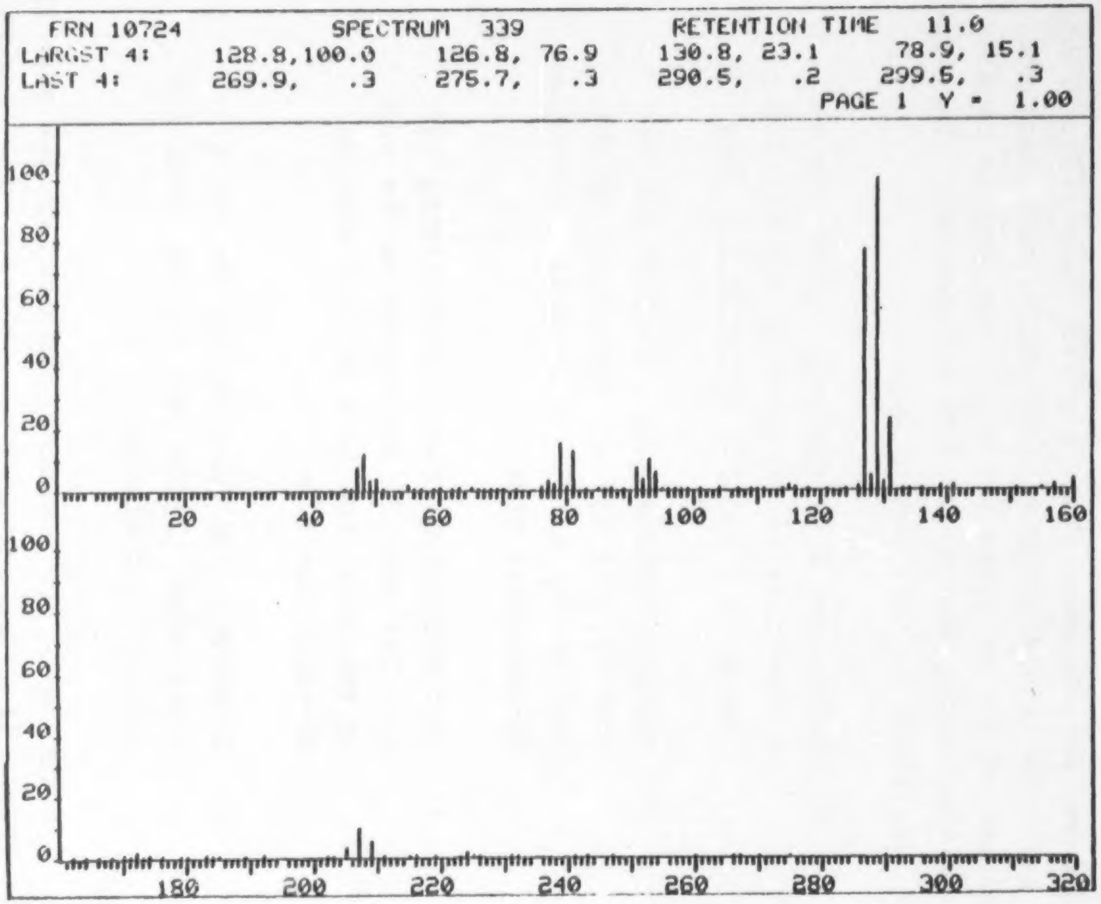
1) Chloroform - an identifying key ion 83 corresponds to the peak on the total ion line at 5.0 minutes GC-retention time

2) Bromodichloromethane - identifying key ions 83, 129 and 127 correspond to the peak on the total ion line at 8.2 minutes GC-retention time

3) Dibromochloromethane - identifying key ions 129 and 127 correspond to the peak on the total ion line at 11.0 minutes GC-retention time

4) Bromoform - an identifying key ion 173 corresponds to the peak on the total ion line at 13.5 minutes

Figure A-7 is a computer print-out of the mass spectrum at point 339 at 11.0 minutes GC-retention time, corresponding to the compound dibromochloromethane of the preceding sample. In this mass spectrum or identifying "fingerprint" for dibromochloromethane, the key ion fragments are expressed in proportionate sizes indicating quantity ratios. Quantities are



```
FRN 10724           SPECTRUM  339          RETENTION TIME    11.0
LARGST 4:     128.8,100.0     126.8, 76.9     130.8, 23.1      78.9, 15.1
LAST 4:       269.9,    .3    275.7,    .3    290.5,    .2    299.5,    .3
                                                            PAGE 1  Y =  1.00
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Figure A-7. Computerized printout of mass spectrum at Point 339 for dibromochloromethane.

normalized such that the most abundant ion fragment arbitrarily equals 100%. Sample ratios must agree with the ratios established for standards of a compound before identification can be confirmed.

Since the GC-MS system is completely computerized, the mass spectral data of other compounds not on the Consent Decree List, but which are possible significant pollutants, can be stored to be examined at a later time.

3.0 ANALYTICAL PROCEDURE FOR ANALYSIS OF INORGANICS

3.1 INTRODUCTION

This section describes the inorganic sampling and analytical strategy for the assessment of wastewater treatment technologies as applied to the utility industry.

Samples were collected from three water streams within each of the plants. These streams included:

1) Cooling tower blowdown (CTB)

2) Ash pond effluent (APE)

3) Plant inlet water

Bench-scale operations of the three technologies assessed (carbon adsorption, reverse osmosis, and chemical precipitation) were applied to the two effluent streams. Plant inlet water was collected to define the quantity of priority pollutants entering the plant.

Grab samples were also collected around an operational full-scale vapor compression distillation unit at one plant. Samples collected included the feed, product, and reject brine.

The following trace elements and water quality parameters were chosen for an analytical laboratory investigation of resulting water samples:

Trace elements

arsenic
antimony
beryllium
nickel
selenium
silver

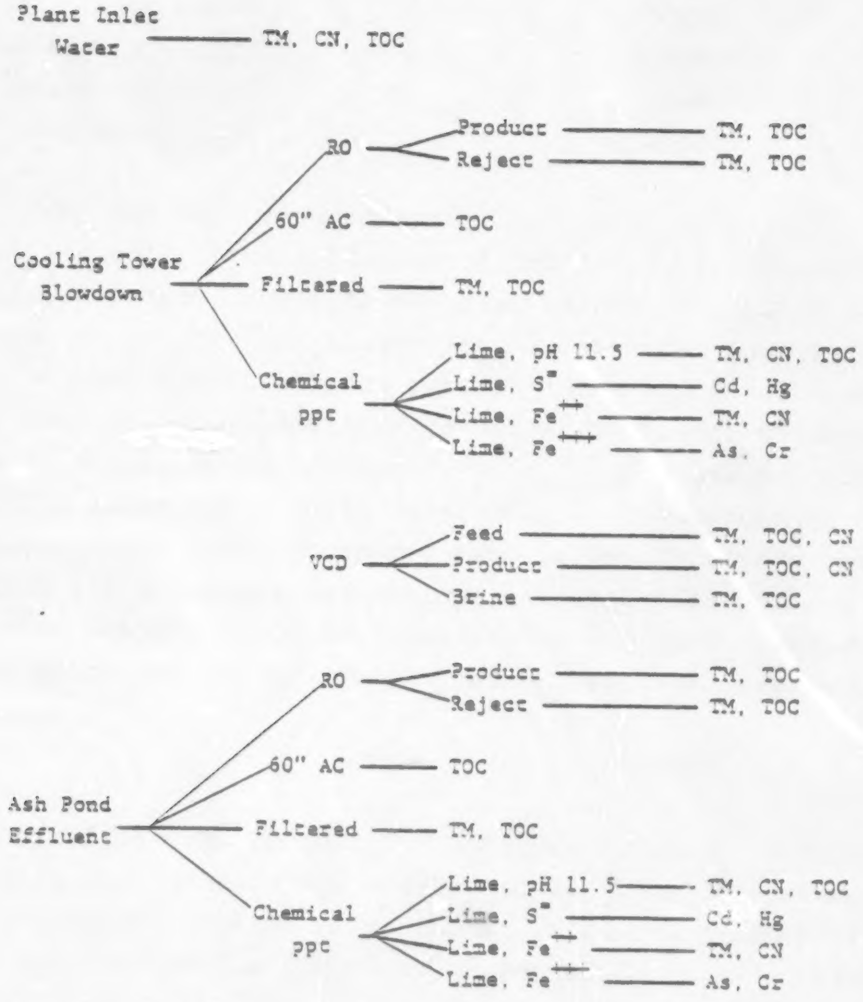
cadmium
chromium
copper
cyanide
lead
mercury
thallium
vanadium
zinc
Total Organic Carbon
Total Suspended Solids
Total Dissolved Solids

The parameters measured were from the EPA list of priority pollutants of industrial effluents. Figure A-8 presents the analytical scheme used for inorganic compounds. The analytical scheme consists of the type of analyses to be performed on the sampled raw water streams and the treated water streams. Complete characterization of each sample for all parameters was not necessary. The focus of the activated carbon treatment study centered on organic adsorption. The total organic content was monitored by measurement of total organic carbon. Chemical precipitation samples were evaluated for trace element removal. Both raw and filtered effluent streams were analyzed to determine trace element content in the suspended solids.

3.2 SAMPLING

Reverse osmosis (RO) samples were collected directly from the RO unit during on-site operation. Initially sampling was monitored using a conductivity meter. Carbon column samples were taken from the column following a line-out time of approximately 1 hour.

Chemical precipitation samples were collected following the jar test procedure performed on-site. The pH of the raw sample was adjusted to the appropriate pH with a lime slurry. Additional coagulants were also added at this time. Following a period of flocculation and settling, the samples were filtered through a 10-micron gravity filter.



Explanation of Abbreviations:

TM = Trace Metals
CN = Cyanide
TOC = Total Organic Carbon
RO = Reverse Osmosis
AC = Activated Carbon
VCD = Vapor Compression Distillation

Figure A-8. Inorganic analytical scheme.

All raw, filtered, and treated (reverse osmosis, carbon adsorption, and chemical precipitation) samples were preserved immediately after collection according to the analysis to be performed. Table A-19 presents the preservative used for the different types of analysis.

TABLE A-19. PRESERVATIVES FOR ANALYSES

Analysis	Preservative	pH
Trace metals	HNO_3, redistilled	<2.0
Cyanide	NaOH, pellets	>12.0
TOC	H_2SO_4	2.0
TDS, TSS	No preservation	

Following colletion and preservation, the samples were stored in polyethylene bottles and transported to the Radian laboratory. During transportation, the temperature of the samples was maintained below 5°C.

3.3 ANALYTICAL METHODS

All trace metal analyses, except selenium, were performed by atomic absorption (AA). Selenium was analyzed by fluorometry following an organic extraction procedure. Cyanide was analyzed by colorimetric procedure. Total organic carbon was analyzed using a non-dispersive infrared spectrophotometer. A standard jar test apparatus was used for the settling data. The instruments used for analysis were:

1) Instrumentation Laboratories Model 351 AA with CTF 555 Flameless Atomizer

2) Perkin-Elmer Model 503 AA Flameless Atomizer

3) Turner Fluorimeter Model 111

4) Coleman Model 124 Double-beam UV-Visible Spectrophotometer

5) Oceanography International Carbon Analyzer

6) Hach Model 15057 Floc Tester

3.3.1 Digestion Methods

Trace metal samples were digested according to EPA protocol. Sample preparation followed the methods described below.

Method A--

A 100-ml aliquot of the sample was transferred to a Pyrex beaker. Five milliliters of 6N hydrochloric acid were added, and the sample was then heated for one hour at 95°C. Following cooling, the sample was diluted volumetrically to 100 ml.

Method B--

A 100-ml aliquot of the sample was transferred to a Pyrex beaker. Three milliliters of 15N redistilled nitric acid and 5 ml of 30% hyrdogen peroxide were added. The sample was heated at 95°C until the volume was reduced to less than 50 ml. After cooling, the volume was adjusted to 50 ml.

The analytical methods for analysis of each element using these digestion techniques are indicated in Table A-20.

TABLE A-20. ANALYTICAL METHODS FOR DETECTION OF METALS

Method A		Method B
Flame[a]	Flameless	Flameless
Be	Be	As[b]
Cd	Sb	Cd
Cr		Cr
Cu		Cu
Ni		Ni
Pb		Pb
Zn		Zn
		Ag
		Tl

[a] If the concentration was near the detection limit for flame AA analysis, reanalysis by flameless AA (graphite furnace) was performed.

[b] Matrix modifications technique.

3.3.2 Trace Metals Analysis

Analysis by standard AA flame techniques was first attempted (Table A-20). If the analytical concentration was below reliable detection limits, the sample was injected into the flameless graphite atomizer attachment of the AA. All flameless analyses were performed on the designated digestion (Table A-20) by direct injection. No preconcentration procedures were used. Arsenic, due to its volatility, was pretreated by adding ammonium molybdate to an acidic aliquot of the samples. This matrix modification technique, producing a more thermally stable arsenic compound, allowed higher charring temperatures for matrix removal.

Table A-21 lists the analytical wavelength used for each element and the atomization program used in the flameless technique.

TABLE A-21. ANALYTICAL WAVELENGTHS IN ATOMIZATION PROGRAM FOR ELEMENTS ANALYZED

Element	Wavelength, nm	Dry, °C	Pyrolize, °C	Atomize, °C
Ag	328.1	100	300	1800
As	193.7	100	1000	2000
Be	234.9	100	1000	2500
Cd	228.8	100	400	2000
Cr	357.9	100	900	1850
Cu	324.7	100	750	1800
Ni	232.0	100	600	1950
Pb	283.3	100	600	1900
Sb	217.6	100	400	2250
Tl	276.8	100	400	1800
V	318.4	100	750	2800
Zn	213.9	100	425	1500

Mercury--

Mercury was determined using a cold vapor technique with the AA. A 100-ml aliquot of the undigested sample was transferred to a BOD bottle. The mercury was oxidized to Hg^{+2} in acidic conditions with excess potassium permanganate. Excess permanganate was removed with hydroxlamine. Stannous chloride was then added to reduce Hg^{+2} to elemental mercury. The mercury vapor was swept through the absorption cell of the AA. The determination was made at a wavelength of 253.6 nm and compared to standards prepared in the same fashion.

Selenium--

The fluorimetric determination of selenium was accomplished by heating a 5-ml aliquot of the undigested sample with dilute HCl. Selenate was reduced to selenite by this procedure. Interferences were masked by the addition of hydroxylamine, EDTA, and formic acid. A fluorescent, photo-sensitive piazselenol was formed by the reaction of the selenite with 2,3-diaminonaphthalene. The complex was extracted into cyclohexane. The organic complex was excited at 369 nm and the resulting fluorescence measured at 522 nm. Concentration was determined by comparison to standard selenium solutions carried through this procedure.

3.3.3 Cyanide and TOC Analysis

Cyanide and total organic carbon were determined by standard techniques. Cyanide was analyzed by colorimetry using a Coleman Model 124 double-beam Spectrophotometer. Total organic carbon was analyzed by a non-dispersive infrared technique using an Oceanography International Carbon Analyzer. Each analysis was performed on specifically preserved samples.

Cyanide--

Cyanide analysis was performed on the sample preserved with sodium hydroxide. A 250 ml aliquot of the sample was transferred to the reaction flask of the cyanide distillation apparatus, Figure A-9. The sample was acidified with 50 ml of 9N sulfuric acid and 20 ml of 2.5N magnesium chloride. The hydrogen cyanide gas was distilled from the flask into 100 ml of 1.25N sodium hydroxide in a gas washing bottle. Following a reflux time of one hour, the absorbing solution was diluted to 200 ml. A 20-ml aliquot of this solution was transferred to a 50-ml volumetric flask. The aliquot solution was buffered with 15 ml

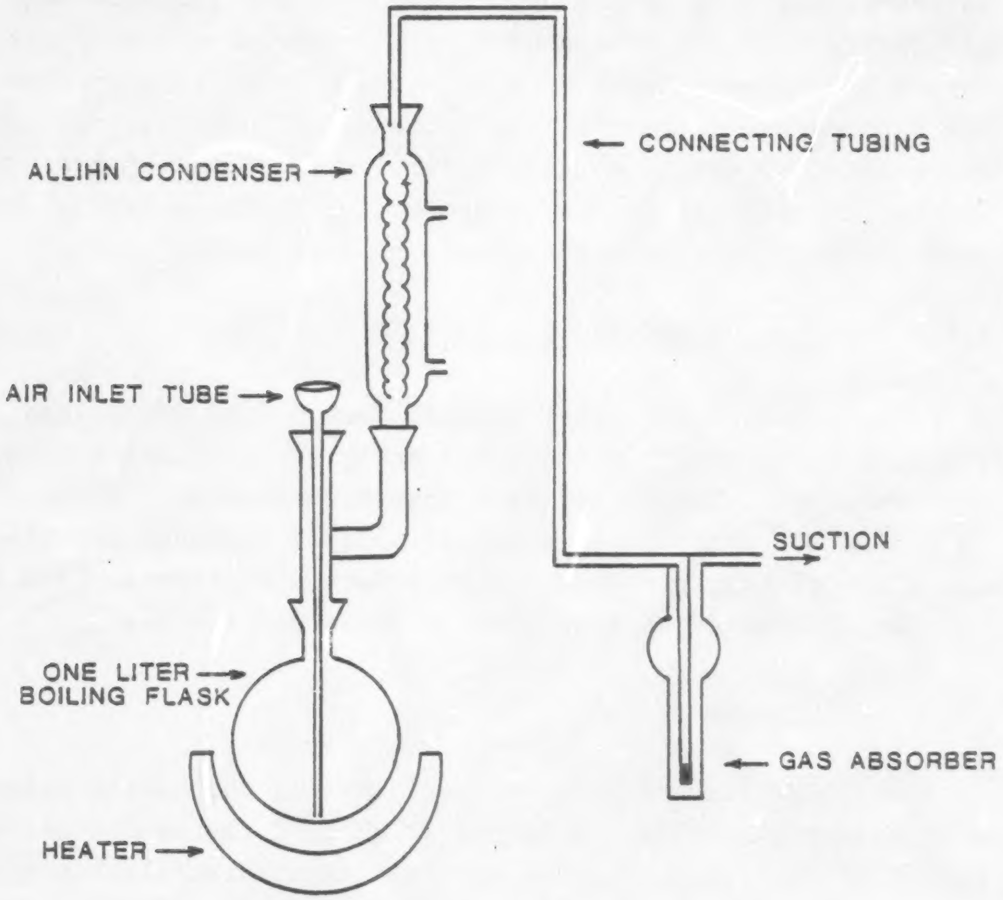


Figure A-9. Cyanide distillation apparatus.

of 1M sodium dihydrogen phosphate and 2 ml of 1% chloramine-T solution were added. Within 30 seconds, 5 ml of the pyridine-barbituric acid were added. The analyte solution was then diluted to 50 ml and the color allowed to develop for 10 minutes. The absorbence was measured at 578 nm with a double-beam spectrophotometer. Concentration was determined by comparison to standards.

Total Organic Carbon--

The organic carbon present in the preserved sample was oxidized to carbon dioxide with potassium persulfate and phosphoric acid. The oxidation procedure was performed in a sealed ampule at an elevated temperature. The resulting CO_2 was measured by passing the gas through the absorption cell of the nondispersive infrared analyzer. Atmospheric CO_2 was excluded and water vapor was removed before the gas entered the cell. The quantity of CO_2 was measured by a recorder equipped with a disc-chart integrater. Peak areas of the sample were compared with the peak areas of standards prepared in the same fashion.

3.4 RESULTS AND ERROR ANALYSIS

High accuracy of the trace metal analysis was assured by analyzing a sample of National Bureau of Standards (NBS) water, SRM 1643, in conjunction with the water samples. Table A-22 gives a comparison between the NBS certified value and the value obtained by Radian. Duplicate digestions and analyses were performed on the plant inlet water, raw cooling tower blowdown, and raw ash pond effluent. The duplicate analyses provided a measure of precision of the analytical techniques. Detection limits and precision data are listed in Table A-23.

TABLE A-22. COMPARISON OF NBS WATER SAMPLE SRM 1643 WITH RADIAN RESULTS

	NBS Value, ng/g	Radian Value, ng/g
As	76 ± 1	86 ± 1
Sb	NL[a]	NA[b]
Be	19 ± 1	16 ± 2
Cd	8 ± 1	7 ± 2
Cr	15 ± 1	14 ± 3
Cu	16 ± 1	22 ± 4
Pb	20 ± 1	18 ± 2
Hg	2[c]	2.7 ± .3
Ni	49 ± 1	53 ± 6
Se	12 ± 1	(8)[d]
Ag	3.4 ± .4	(5)
Tl	NL	NA
V	50 ± 1	(53)
Zn	65 ± 3	(59)

[a] NL = Not Listed

[b] NA = Not Analyzed

[c] Not certified due to possible container contaminant

[d] ( ) Only one value available

TABLE A-23. DETECTION LIMITS AND ACCURACY OF DATA FOR INORGANIC ANALYSES

	Detection limit, ppb	Accuracy 5xDL
As	1.0 = 100% if ≤ 5 ppb	= 20% if > 5 ppb
Sb	1.0 = 100% if ≤ 5 ppb	= 20% if > 5 ppb
Be	0.5 = 100% if ≤ 2.5 ppb	= 20% if > 2.5 ppb
Cd	0.3 = 100% if ≤ 2.5 ppb	= 20% if > 2.5 ppb
Cr	2.0 = 100% if ≤ 10 ppb	= 20% if > 10 ppb
Cu	4.0 = 100% if ≤ 20 ppb	= 20% if > 20 ppb
Pb	3.0 = 100% if ≤ 15 ppb	= 20% if > 15 ppb
Hg	0.2 = 100% if ≤ 1 ppb	= 20% if > 1 ppb
Ni	0.5 = 100% if ≤ 2.5 ppb	= 20% if > 2.5 ppb
Se	2.0 = 100% if ≤ 10 ppb	= 20% if > 10 ppb
Ag	0.2 = 100% if ≤ 1 ppb	= 20% if > 1 ppb
Tl	1.0 = 100% if ≤ 5 ppb	= 20% if > 5 ppb
V	4.0 = 100% if ≤ 20 ppb	= 20% if > 20 ppb
Zn	2.0 = 100% if ≤ 10 ppb	= 20% if > 10 ppb
CN^-	1.0 = 100% if ≤ 5 ppb	= 20% if > 5 ppb
TOC	20 ppm = 100% if ≤100 ppb	= 20% if > 100 ppb

From previous calculations, analytical accuracy decreases as the results approach the detection limit. Generally, the accuracy is ±100% if the result is within five times the listed detection limit. For concentrations in excess of this value, the accuracy is ±20%. Most of the results obtained were near the detection limit. These values are well below published levels of trace metals contamination, such as those shown in Table A-24.

Detection limits are listed for cyanide and TOC data. Standard cyanide samples were not available. However, recovery studies performed previously have shown greater than 95% recovery of cyanide from the distillation. Standard TOC samples were not available. Replicate analyses of samples and multiple standards were included to insure analytical quality.

TABLE A-24. WATER QUALITY CRITERIA

	QUALITY CRITERIA FOR WATER[a]					
			Freshwater			
	Domestic Water Supply	Irrigation	Soft	Hard	Marine	Remarks
As	50	100				All values in ppb, unless otherwise noted
Sb						
Be		100 500, soil pH>7	11	1100		
Cd	10		0.4 - 4.0	1.2 - 12	5	Freshwater standards, species dependent
Cr	50		100	100		
Cu	1000					.1 of 96 hr LC_{50} for aquatic
Pb	50					.01 of 96 hr LC_{50} for aquatic
Hg	2.0		.05	.05	.10	
Ni						.01 of 96 hr LC_{50} for aquatic
Se	10					
Ag	50					.01 of 96 hr LC_{50} for aquatic
Tl						.01 of 96 hr LC_{50} for aquatic
V						
Zn	5000					.01 of 96 hr LC_{50} for aquatic
N	5		5	5	5	
TDS	250 ppm					For Cl^- and $SO_4^=$ salts

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[a] EPA, "Quality Criteria for Water", EPA-440/9-76-023. Washington, D.C., 1976.

REFERENCES

A1. Environmental Protection Agency, Environmental Monitoring and Support Laboratory. Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants, revised. Cincinnati, Ohio, April 1977.

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